

STUDIES OF
RIGID PVC PIPES
BY
SCANNING ELECTRON MICROSCOPY

LENNART JOHANSSON

DISSERTATION 1984

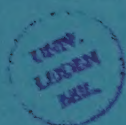


DEPARTMENT
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av

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STUDIES OF RIGID PVC PIPES BY SCANNING ELECTRON MICROSCOPY

Abstract

Fracture surfaces in rigid PVC pipes subjected to internal pressure tests were investigated by scanning electron microscopy. This showed that the fractures were initiated by particles, (either unevenly dispersed solid additives or impurities), regions of bad gelation or surface defects. Even in experiments where efforts were made to produce pipes free from particles, fracture initiation by particles, in this case soft, rubber-like ones was the most common cause of fracture initiation. The broad distribution in time-to-failure observed in the internal pressure tests most probably can be referred to the presence of different fracture mechanisms and physical aging during testing. In some fracture surfaces obtained at high internal pressures (40 PMA at 20°C or 18 MPa at 60°C), unbroken primary particles and almost intact grains of PVC were found. This indicates that there exist certain conditions of stress or strain rate which may give information, by way of the fracture surface appearance, on the degree of gelation. Back-scattered electron imaging in the scanning electron microscope was found to give information on the influence of the processing conditions on the distribution of lead in lead-stabilized rigid PVC pipes. A combination of electron irradiation and treatment with methylene chloride made it possible to quantitatively determine the level of gelation for well-gelatinized PVC pipes.

Key words

Poly(vinyl chloride), PVC resin, level of gelation, fractography, SEM, internal pressure test, impact test, tensile test.

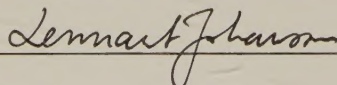
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To my wife, Danit

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STUDIES OF RIGID PVC PIPES BY SCANNING ELECTRON MICROSCOPY

This thesis consists of the summary and the following papers, referred to in the text by their Roman numerals.

- I SEM studies of fractures of rigid PVC pipes.
Lennart Johansson and Bertil Törnell.
Acta Polytech. Scand., Ch 142,
Helsinki 1980.
- II The effect of processing conditions and resin structure on impact strength; long-term performance and fracture morphology of rigid PVC pipes.
Lennart Johansson, Bertil Törnell and Lennart Agren.
Acta Polytech. Scand., Ch 150,
Helsinki 1982.
- III The scattering in time-to-failure for rigid PVC pipes produced from a particle-free formulation.
Lennart Johansson and Bertil Törnell.
Subjected for publication.
- IV Information about incomplete gelation in rigid PVC from SEM studies of fracture surfaces.
Lennart Johansson and Bertil Törnell.
Subjected for publication.

V Tensile creep-tests, internal pressure tests and scanning electron microscopy of electrical conduits of PVC.

Lennart Johansson and Bertil Törnell.

Subjected for publication.

VI The distribution of lead in lead-stabilized rigid PVC pipes, as studied by scanning electron microscopy.

Lennart Johansson and Bertil Törnell.

Subjected for publication.

VII A combination of electron irradiation and the methylene chloride test for obtaining the level of gelation for rigid PVC pipes.

Lennart Johansson.

Subjected for publication.

The summary is divided into two parts. Part I briefly describes different polymerisation processes for PVC production and the morphology of the corresponding PVC resins. It also deals with questions regarding the effect of the formulation and processing conditions on the quality of the processed PVC. The use of scanning electron microscopy in the study of PVC fracture surfaces is outlined, as is the effect of different parameters on the fracture surface appearance. Part II consists of a summary of the papers.

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SUMMARY

Part I

Polyvinyl chloride (PVC) has been produced commercially since the 1930s and is today a major polymeric material. Around 50 % of the production is used in building and construction applications. The largest single product is rigid pipes for water and sewage lines. The market share for pipes of PVC has increased rapidly during the last decades. However, the long term behaviour is not fully understood and premature failures are occasionally reported (1-3). Further testing of the mechanical properties are therefore essential. A prediction of the service life is usually attempted by extrapolation in a plot of log stress versus log time-to-failure. The prognostic value of such a prediction might be increased by considering results from fractographic studies of the tested samples. By using scanning electron microscopy it is possible to reveal the reasons for fracture initiation and to study the different fracture mechanisms. This work will show that the scanning electron microscope can play an important role as a research tool in the study of the long time behaviour and description of the internal structure of PVC.

POLYMERISATION PROCESSES FOR PVC

The first process used for the production of PVC was emulsion polymerisation. The product obtained, E-PVC, was found to be suitable for paste-making due to its ability to form a fluid mixture with an equal weight of plasticizer (4).



The emulsion process is still in frequent use for preparing paste resins.

Suspension polymerisation requires lower amounts of additives than the emulsion process and therefore produces purer resins. It has become the most important process for the manufacture of PVC. A typical formulation consists of VCM, water, suspension stabilizers, buffer and a monomer-soluble initiator. The polymerisation is carried out in an autoclave at temperatures between 50 to 70°C. The process is strongly exothermic. For quality reasons, the conversion is never driven to completion and residual VCM is carefully removed from the resin. The product, S-PVC, consists of porous grains which are recovered from the slurry by filtration.

The bulk process is seemingly less complicated as it involves only monomer and initiator. The process is driven in two steps. In the first one, primary particles are nucleated and coagulated into loosely packed grains. In the second step, these grains grow and become more compact. As in emulsion and suspension polymerisation, the molecular weight is determined by the polymerisation temperature. The grain size is controlled by the agitation speed during the first step. The conditions for the two steps are quite different and they are carried out in two separate reactors.

FROM RESIN TO A PRESSURE PIPE

The processing of PVC is quite different from that of other

thermoplastics. The main reasons for this are the low thermal stability of PVC and the fact that PVC is slightly crystalline and has a melting temperature of about 225°C, which is higher than the normal processing temperature. A pressure pipe of PVC might contain up to ten different components. The typical formulation consists of resin, lubricant, stabilizer, filler and pigments. The dominating component is the resin. In pipe production a suspension resin is normally used. The molecular weight or the K-value of the resin is of great importance for the quality of the pipe. An increase in the K-value increases impact strength and improves the long-term pressure resistance (5,6) Resins with high K-values are more difficult to process.

The stabilizing system protects the resin from decomposition during processing. Lead stabilizers are normally used in Europe. This is forbidden in the USA due to health and environmental considerations. Instead, tin stabilizers are frequently used.

The lubricants are divided into two classes; external and internal. The external lubricant reduces the friction between the melt and the metal surfaces of the extruder. The internal lubricant reduces the amount of heat build-up within the grains during processing (7). The type and amount of the internal lubricants are most important because they control the gelation process and thereby the end products of the processed PVC.

A filler, usually calcium carbonate, is added in small amounts mainly in order to improve processing.

PVC-resin in powder form is mixed with the additives in a high speed, powder mixer at a temperature about 100°C. During this process the additives become evenly distributed over the resin grains. The dry powder blend is cooled in a second mixer and is then fed into a single or twin-screw extruder. In the extruder, the grains are broken down by heat and friction and the resin forms a melt which is shaped into a pipe when passed through the die.

The quality of the pipe is related to the level of gelation. This in turn depends on the processing temperature, shear, residence time and amount of lubricant. Fluctuations in the raw material might affect the pipe quality.

THE MORPHOLOGY OF PVC

The different polymerisation processes give resins with different morphology. A typical suspension resin consists of porous particles with diameters in the range of from about 100 to 200 μm (8). The particles normally have an outer skin which is formed during the initial stage of the polymerisation process. A skinfree S-PVC resin was recently introduced by the Swedish company, KemaNord. Microscopic studies show that S-PVC grains have a rather complicated morphology. They seem to be built up from irregularly shaped "primary particles" (about 1-2 μm in size) and agglomerates of such particles with different sizes. The so-called "primary" particles are most probably formed by agglomeration of the very small (about 0,1 μm) particles that are formed during the first stage of the polymerisation, i.e. up to

some percent conversion. A system for classification of the different morphological entities observed in S-PVC grains has been introduced by Faulkner (9). Recently, another system was agreed upon at the Lyon-Villerubanne congress (10).

For many years it was believed that the resin was fully melted during processing. The first evidence of a particulate structure in processed rigid PVC was reported by Berens and Folt (11). They found flow units $\sim 1 \mu\text{m}$ in size in extrudates from a constant-load capillary rheometer. The idea that the flow units in PVC processing are small particles rather than molecules now seems to be generally accepted. The appearance of particles of PVC in processed goods suggests that the gelation process involves another mechanism besides comminution. According to Allsopp (12) it consists of compaction, densification, fusion and elongation of the grains. This interpretation was based on experiments using an extruder where the mechanical treatment of the resin was less aggressive than in a Brabender Plasticorder, an instrument often used in studying PVC processing. The gradual change in structure during processing in a Brabender Plasticorder can be seen as peaks in the temperature-torque curves (9). These peaks are associated with the break-down of the PVC grains.

As compared to most S-PVC resins, M-PVC resin grains are skinless and have a nearly spherical shape.

Most E-PVC resins are recovered from the latex by spray drying. This gives very compact grains with very little porosity. Such resins are not suited for extrusion. Occasionally E-PVC resins are recovered by coagulation of the latex. Such resins may become porous and can be used as extrusion resins.

MORPHOLOGY STUDIES OF PVC BY SEM

The introduction of the scanning electron microscope (SEM) has provided a new technique for morphological studies of polymers (13). It is mainly the high resolution in combination with the large depth of focus which makes the SEM so powerful. SEM studies require no preparation technique other than coating the samples with a conducting layer in order to avoid charging artefacts during investigation. When SEM is used in its normal operation mode, a secondary electron detector is also employed, which gives a good topographic contrast.

It is also possible to detect the back-scattered electrons, the intensity of which varies with atomic number. The detector thus gives an image which in the case of flat specimens is a mapping of the atomic number contrast. The back-scatter electron detector can be used together with an environmental cell (14). It consists of a modification of the vacuum system and enables pressures of between 0.1 torr and 1 torr to be maintained in the specimen chamber, while the beam is generated in the high vacuum electron optics column. The gas molecules in the sample chamber dissipate

the electric charge on the sample and the specimen can be examined without the need for conductive coating. This is of great importance in the study of polymeric materials.

By using an energy dispersive X-ray analyzer connected to the microscope, it is possible to determine the composition of impurities and additives in the specimen (15).

The porosity of the grains may be investigated by secondary electron imaging after cutting or breaking the grains. The internal structure may also be studied by TEM, but it requires embedding of the sample (16,17). The smallest morphological entities, the micro-domains, can only be studied in a TEM (18). The micro-domains may easily be thermally damaged since high beam fluxes are required in this case. The nature of the micro-domains may therefore be disputed. The scanning transmission electron microscope (STEM) might give further evidence as to the existence of the micro-domains since less beam damage is obtained in this type of microscope.

It is rather complicated to study the break-down of the grains during extrusion. One way of doing this is to dismantle the extruder for inspection of the fusion in the different zones. Uitenham and Geil followed the gradual break-down of grains down the screw in an extruder until the grains disappeared into the melt (19).

Only a few investigations of the internal structure of extrudates have been reported. These kinds of investigation

require rather complicated preparation techniques. Ion etching of a number of cross-sections of extrudates showed a particulate structure (20).

The boundary between morphology and fractography is fuzzy. Sometimes it is necessary to obtain fractured samples in order to study the morphology. Fractography covers interpretations of the failure mechanism and characteristic fracture patterns and is therefore discussed in a separate paragraph.

FRACTOGRAPHY OF PVC

The interpretation of the fracture surfaces is rather complicated since many parameters affect the fracture appearance such as:

- rate of loading
- crack velocity
- processing temperature
- level of gelation
- molecular weight
- orientation
- testing temperature
- particles
- physical aging

In general, the surface roughness seems to increase with the crack propagation velocity in rigid polymers (21). However, elastomers show a smoother surface with increasing crack velocity (22). This indicates that there is no universal correlation between roughness and crack velocity. However, there exists a correlation between fracture surface

roughness and the hysteresis ratio for different materials and temperatures (22). High hysteresis results in a low degree of roughness. It is demonstrated that the strain required to propagate the fracture increases with the hysteresis ratio.

The rate of loading, which may be varied within a broad range, and the testing temperature may have a great effect on the appearance of the fracture surface. The slow bend test shows a tendency towards brittle fracture at very low temperatures. An increase in the testing temperature indicated signs of plastic deformation in PVC around -60°C . At still higher temperatures (0°C) the fracture became ductile and the fracture surface showed a fibrous texture (23).

In the impact test, the crack propagates in larger steps and the extent of plastic deformation is smaller than in the slow bend test (23). An impact test might show plastic deformation at low testing temperatures if the samples tested are processed at a high melt temperature (210°C) (19). It has been reported that fracture surfaces from impact tests of rigid PVC pipes at 20°C show differences in morphology for different levels of gelation (24). At a gelation level around 44-68 % as measured by capillary rheometry, a maximum in deformation is obtained.

As regards fatigue fractures, an increase in molecular weight serves to enhance craze stability which delays the break-down of the craze. In addition, the enhanced craze stability allows the void growth to proceed further,

resulting in a more mottled fracture appearance (25).

Physical aging of PVC, i.e. aging at temperatures ranging from T_g to $T_g - 50^\circ\text{C}$, leads to embrittlement. This is reflected in the appearance of the fracture surface which shows less filament formation and an overall smooth surface (cf. Paper III).

Orientation of the PVC molecules increases resistance to crack propagation perpendicular to the direction of orientation. The oriented rigid PVC pipe "Superpolyorc" shows quite a different fracture appearance than a conventional pipe (26).

The fracture surfaces contain characteristic patterns which are representative of the different failure modes. Hence, a brittle failure might show hackle marks (27) which converge towards the point of fracture initiation. Sometimes crack-front traces mark crack arrest due to unloading at the crack tip. In this case it is also easy to find the origin of the fracture.

A characteristic pattern for subcritical crack-growth in PVC is the mirror area (28). It appears smooth as a mill-pond at low magnifications but under the scanning electron microscope it is seen that it contains filaments. According to Mandell et al the fibrills or the filaments disappear when calcium carbonate is used as a filler (29). In the present work filaments were found in all fracture surfaces even when calcium carbonate was used as a filler. The reason

for the absence of filaments, was thus probably not due to the presence of fillers in the studies by Mandell and coworkers. It might rather be a consequence of the fact that their material was very well annealed (cf. Paper III)

The circular boundary of the mirror area demarcated the point at which the subcritical crack propagation rate terminated. The area of catastrophic crack propagation showed an increased surface roughness.

Fatigue fracture surfaces of PVC display two characteristic patterns. The most well-known of these consists of striations formed at high ΔK levels (30) as a result of crack arrests at the end of each loading cycle. The distance between adjacent striations increases with an increase in ΔK . The other pattern appears at low ΔK and consists of fracture bands perpendicular to the direction of crack propagation (25,30). These bands are formed by discontinuous crack extension through a craze formed in front of the crack and consist of microvoids which decrease in size in the direction of crack extension. The size of the bands is believed to be equal to the length of the plastic zone in front of the crack tip.

SUMMARY

Part II

The internal pressure resistance test.

The long-term behaviour of rigid PVC pipes can be predicted by subjecting the pipes to an internal pressure that exceeds service requirements. The outside pipe wall diameter and minimum wall thickness are measured and from these data the internal pressure, P , corresponding to a certain hoop stress, is calculated from the equation:

$$P = \sigma \frac{2e_{\min}}{d_{m,\max} - e_{\min}}$$

where σ = the circumferential stress (N/m^2)

$d_{m,\max}$ = the maximum mean outside diameter (mm)

$e_{\min}$ = the minimum wall thickness (mm)

According to ISO 1167 - 1973 pipes should not be tested within 1 h following production. Furthermore, they must be conditioned at the desired testing temperature for 1 h. The pipes may be put in test position in three different ways (31), which affect the stress field. Water or gas may be used as pressure media. Water is normally chosen because it is safer to handle. The internal pressure test gives the time-to-failure at a certain stress level. Many pipes are often tested in parallel and the time-to-failure is taken to be that when the first one fails.

The results from the internal pressure test are normally presented in a diagram which gives the relation between

the hoop stress, which is twice the axial stress, and the time-to-failure. The data are presented either in a log-log diagram or in a lin-log diagram. The use of a lin-log diagram is in agreement with the Eyrings' rate theory (32). A prediction of the service life is usually attempted by extrapolation from the diagrams.

Paper I

The fractured samples from the internal pressure test are often discarded. However, the fracture surfaces may contain information on the processes leading to failure, and this information may be of use in elucidating the properties of the tested material. Hence, a study by scanning electron microscopy of fracture surfaces after pressure testing of rigid PVC pipes was performed.

The fracture surfaces were investigated with a light microscope and a scanning electron microscope (JEOL JSM-U3). The pipe samples were sputter coated with gold prior to fractographic investigations. Analyses of the surfaces were carried out with an energy dispersive X-ray spectrometer (PGT 1000) attached to the scanning electron microscope.

The study showed that one of the most common reasons for fracture initiation was the presence of different kinds of particles. Analyses with the X-ray spectrometer made it possible to divide the particles into two groups. The first contained particles which could be identified as unevenly dispersed additives.

In many fracture surfaces, calcium appeared as a major component of the particles. This indicates that filler agglomerates may have been responsible for fracture initiation.

The second group contained foreign particles, i.e. particles with a chemical composition different from that of the components in the formulation. One such particle consisted of twisted threads with a diameter of 3-5 μm . Microanalyses of the threads indicated that they were fillings from the extruder mixed with some additives. As the extruder is worn down during processing it is not surprising to find small particles in the extruded pipes.

A bluish-green particle was observed in the fracture surface of another sample. Microanalysis indicated the presence of chlorine and copper in the particle. It is possible that the crystals seen in SEM were formed by reaction between a copper-containing impurity and hydrochloric acid evolved during the test period.

Based on results from transmission electron microscopy (17) it was concluded that inhomogenous gelatinization was the cause of failure for one of the samples. No rational explanation for the relatively short time-to-failure for this sample could be obtained by scanning electron microscopy.

The experimental material available at the time of this study thus indicated that the dominating reason for fracture initiation was not a low level of gelation but rather the

presence of particles, either filler particles or particles present as impurities.

Paper II

To gain more information on fracture initiation in PVC pressure pipe, a study was made of the fracture surface appearance of samples differing in their level of gelation. The level of gelation was varied by using formulations containing different amounts of lubricant. Experiments with pipes prepared from different resins were included in this study.

The pipe samples were prepared using four twin-screw extruders with different capacities. This was done in order to permit a resolution of resin and machine factors.

The results indicated that the ability of the pipes to resist internal pressure over a long period of time increased with an increase in the level of gelation, i.e. with a decrease in the amount of lubricant. The methylene chloride test showed that large amounts of lubricant indeed resulted in bad gelation.

An interesting result obtained in this work was the occurrence of a knee in the log stress versus log time-to-failure curves for pipes containing large amounts of lubricant. According to a literature survey by Terselius (6), such knees have been observed only in the case of pipes prepared from resins with low K-values and low levels of gelation. Thus, at a K-value of 68, which was used in the present work, curves of this type have not previously been reported to change slope at low stress levels. The present results indicate, however, that such a change in slope may indeed occur even at high K-values. This means that the prognostic value of the common 1000 h tests may be lower than expected for samples with a low degree of gelation.

Change in slope has previously been taken to indicate a transition from a ductile to a brittle failure. This transition is assumed to be due to a change in fracture mechanism from creep-propagation to crack-propagation. The same explanation has been offered for the existence of a knee in corresponding curves for polyethylene pipes (33).

The fractographic studies indicated that in this experimental material many of the fractures were initiated by inclusions. These showed up as red and yellow areas in the light microscope. Most of the inclusions had a particle size ranging between 50 and 100 μm and were found in pigmented pipes only. According to energy dispersive X-ray analysis, chromium and lead were the only foreign elements detectable in the inclusions. This proved that they consisted of agglomerates of the red and yellow components of the pigment used.

One of the pigmented pipes tested in this work contained about 100 growing cracks, which were mainly initiated by pigment agglomerates. Several of the pipes tested also contained growing cracks with pigment agglomerates. It is obvious therefore, that pigment agglomerates often caused fracture initiation. The results thus demonstrate the need for great caution in choosing and storing pigment compounds.

Particles containing lead as the only detectable element were found in the fracture surfaces of both pigmented and unpigmented pipes. These particles originate from the stabilizer. Although they were small, 1-20 μm , fracture initiation appeared at the particle/matrix interface.

Not all fractures, however, were initiated by particles. In some cases, a low level of gelation or notches seemed to be responsible for fracture initiation as semi-elliptical surface cracks were found in the fracture surfaces. According to fracture mechanics, a semi-elliptical surface crack is considered to be a more severe flaw than an internal crack of the same size, due to the fact that a correction term for the free surface must be included in the calculation of the stress intensity factor. In addition, water penetrating the crack during testing might influence the crack-propagation rate. As expected, a shorter time-to-failure was obtained for a sample with a semi-elliptical surface crack compared to a sample that failed within the pipe wall. Semi-elliptical surface cracks were also found in samples 3, 5 and 8 (Paper I) and these also exhibited a short time-to-failure.

The reason for the initiation of semi-elliptical surface cracks may be a low level of gelation (sample 5, Paper I) or notches formed during the extrusion process, i.e. by the die or mandrell. A high plastic deformation will reduce the effect of a notch as a possible site for fracture initiation, i.e. plastic deformation will be favoured over crack-propagation. The maximum effect of a notch will therefore be observed either on a high stress/short time-to-failure test or at a low stress/long time-to-failure test where brittle failures are encountered.

For thick-walled pipes the failure would be expected to start at the internal pipe wall due to the stress distribution. In an investigation of a number of thick-walled pipes, we were surprised to find, however, that the failure was initiated at the external pipe wall. This indicates that severe flaws must be operative to an extent that was previously not realized since the combined effect of compressive stresses at the external pipe wall and the stress distribution is to decrease the effect of notches.

Paper III

As was discussed above, most of the failures studied were initiated by particles. With the original aim of studying the scatter in time-to-failure under conditions that would exclude fracture initiation by particles, a study was carried out using pipes prepared from a "particle-free" formulation.

The pipes (110x5.3 PN 10) were produced from a skinless suspension resin, Pevikon 688, using a PVC-soluble, tin-

based stabilizer. Fillers or pigments were not added in order to keep the number of foreign particles at a minimum.

Despite the efforts to make pipes free from particles, most failures were initiated by particles even in this study. These were of a completely new type, however. The particles contained sulphur, chlorine, calcium, titanium and zinc and were rubber-elastic. The results strongly indicated that these soft particles represented serious flaws. Soft particles may be more serious than rigid particles of the same size, and have an effect comparable to that of the pigment agglomerates discussed in the preceding section. It is possible that these soft particles were formed due to the absence of calcium carbonate. The calcium carbonate filler normally used may serve as an adsorbent for impurities and thereby prevent the formation of soft particles by agglomeration of insoluble impurities.

The results obtained strongly suggested that the time-to-failure is determined both by the time for fracture initiation and the rate of fracture propagation. This conclusion was based on the following considerations. The smooth mirror area observed around the particles was formed during crack propagation. Furthermore, the boundary of the mirror area gives the position at which the subcritical propagation terminated and the crack propagation began to accelerate. Moreover, the size of the mirror area increased with the time-to-failure and its fine structure changed from a rough to a smooth texture with increasing time-to-failure. In

addition the structure of the mirror area in one and the same pipe was finer in a growing crack than in the crack that lead to failure. These observations may be explained as a result of physical aging of the PVC material during the time up until the point of fracture initiation. The increase in the size of the mirror area is thus in agreement with the assumption that the strength of the pipe material increased with time during annealing at 60°C . Annealing of a pipe sample for 500 h prior the internal pressure test resulted in a brittle failure. The results clearly show that a test temperature of 60°C is too close to the glass-transition temperature for effects of physical aging to be neglected.

Based on obtained results, a possible mechanism for particle-initiated fractures was outlined as follows.

A mirror area is created around the particle if the requirements for the energy release rate ($G_i < G < G_{1c}$) (34) are fulfilled. This occurs at time t_1 (35), a parameter which depends on the mechanical properties, size, location and orientation of the particle, the adhesion between particle and the matrix and the stress level. T_1 is probably also affected by aging at temperatures above $40\text{--}50^{\circ}\text{C}$. The mirror area reaches a critical size at t_2 . The major factors affecting the time $(t_2 - t_1)$ are the stress level, the size of the pipe wall, the temperature (36) and the annealing time. The time-to-failure (t_3) might almost coincide with t_2 since the crack speed increases rapidly at t_2 . It is likely that $(t_3 - t_2)$ is fairly small as compared to t_2 (35).

According to Niklas and Kausch (37), crack propagation does not affect the lifetime of a pipe. This statement is not generally valid. The results presented in Paper II for a high quality pipe ($\sigma = 17, 4100$ h) containing about 100 growing cracks indicate that the time required for a growing crack to reach its critical size is not negligible in comparison to the time-to-failure. Fig. 1 shows the relation between the size of the particles found in the fracture surfaces and the diameter of the mirror area surrounding a particle. It seems that the time for fracture initiation decreased with an increase in particle size. The largest particles were found in the two cracks which had penetrated the pipe wall and caused the actual failure.

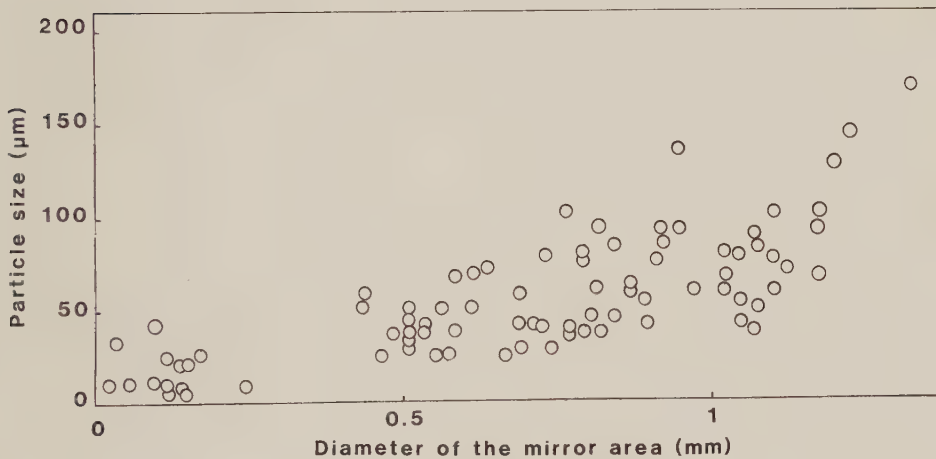


Figure 1. Particle size vs. diameter of the mirror area for growing cracks in a rigid PVC pipe.

In none of the fracture surfaces investigated so far have we ever been able to observe structural details which could be related to the structure of the original PVC resin particles. However, indications that such structures may be present in PVC pipes had previously been obtained by transmission electron microscopy (17).

In a series of pressure tests carried out at a wide range of stress levels, almost entirely intact grains and seemingly undamaged primary particles were found in fracture surfaces formed at an unusually high stress level (42.5 MPa at 20°C and 18 MPa at 60°C). These results indicated that it might be possible to detect incomplete gelation in rigid PVC by SEM studies of fracture surfaces if these were formed in experiments carried out at a suitable stress level or at a certain strain rate.

The scattering in time-to-failure

The results from internal pressure tests indicate that the scattering in time-to-failure is dependent on several parameters:

- testing conditions
- pipe processing
- number and severity of flaws
- failure modes
- aging during testing

The tests are carried out at a constant temperature and pres-

sure and it has been demonstrated that fluctuations in these two testing parameters may increase the scattering in time-to-failure (31). Specimens from a set of pipes contain a large number of flaws differing in their severity. The number and severity of the flaws determine the fracture strength. Typical flaws may be particles, areas of low level of gelation and surface notches. Different kinds of flaws may lead to different failure modes, which contribute to the scattering in time-to-failure. Physical aging during the time until fracture initiation increases the strength of the pipe material, which also increases the scattering in time-to-failure.

Statistical analysis of fracture data

The scattering of the time-to-failure is often described by different distributions. For PE-pipes, Weibulls and log-normal distributions are often used with good results (38). A Gaussian distribution is not applicable since the distributions are often skewed (35).

When fracture is described as a statistical event, it is often assumed that no aging occurs during testing. If the material properties of the pipes are time dependant, however, this factor must be considered when selecting a life-time distribution model.

The hazard function describes how the probability of failure changes with time (39). The Weibull distribution has a hazard function of the type:

$$h(t) = \lambda \cdot \beta (\lambda t)^{\beta-1}$$

Depending on the parameter β , the hazard function may be monotone increasing ($\beta > 1$), decreasing ($\beta < 1$) or constant for $\beta = 1$. Use of the Weibull distribution has become quite frequent due to its mathematical simplicity.

Paper V

The results obtained in Paper IV were followed up by an investigation using electrical conduits prepared from a mixture of suspension and emulsion PVC resin. This type of pipe was chosen because a previous study in this laboratory (17) had indicated that the emulsion PVC particles did not melt completely during processing of such a formulation. It could be expected, therefore, that this type of sample contained some inhomogeneities which might show up in fracture surfaces formed at certain high stress levels.

Two sets of pipes, with different levels of gelation were subjected to internal pressure tests at a constant pressure and tensile tests at a constant load.

The ability to withstand internal pressure was found to be slightly reduced by an increase in the amount of lubricant. This is in agreement with the expected effect of decreasing the level of gelation by increasing the amount of lubricant.

The appearance of the fracture surface differed with the lifetimes of the pipes. At the highest stress levels tested,

both the swelling of the pipes and the nature of the fracture indicated a ductile failure. At a slightly lower stress level, the fracture surface contained areas with a peculiar skin-like structure. The origin of this structure is not obvious. For the lowest stress level, an area of subcritical crack-propagation appeared and the skin-like structure disappeared.

An increased amount of lubricant resulted in a lower initial tensile creep-rate. This was somewhat unexpected as a lower level of gelation has been reported to result in an increased creep-rate.

Annealing, which led to a drastic decrease in the creep-rate, also gave a longer lifetime and a lower ultimate elongation. In this respect, the effect of annealing is similar to that obtained by decreasing the load.

The skin-like structure was not observed in the fracture surfaces obtained in the notched tensile tests at constant load.

The difference in fracture appearance between the two test methods is probably due to orientation effects and to differences in the site of fracture initiation and differences in the stress fields.

Paper VI

The results from Paper II indicated that failure may be initiated at the surface of lead stabilizer particles. There are also literature data pointing to differences in the fracture behaviour of tin and lead stabilized PVC (40), which might depend on the fact that the lead stabilizer consists of insoluble particles whereas the tin stabilizer dissolves in the polymer. A study of the distribution of lead in lead stabilized PVC was, therefore, deemed very important.

It is possible to observe lead-containing particles using transmission electron microscopy. This technique, however, requires ultrathin sectioning and gives information from very small areas only. Much more convenient is the use of scanning electron microscopy.

The samples studied were rigid PVC pipes prepared from a formulation based on a suspension resin (Pevikon S 688 from KemaNord) and a lead stabilizer. Two sets of samples were used. In one set the level of gelation was varied by using different amounts of lubricant, in the other the level of gelation was varied by processing at different mass temperatures.

The pipes were cut radially by a diamond saw so that flat, smooth surfaces were obtained.

Back-scattered electron imaging in the scanning electron

microscope made it possible to study the distribution of lead in the sample surface. The back-scattered electrons were detected by a Robinson detector (41), whose signal increases with the average atomic number of the specimen. The large atomic number difference between lead and chlorine made it possible to see lead-containing domains as bright areas against a darker background.

The results showed that the distribution of lead was affected by processing conditons. Almost the same particle size distribution was obtained at the lowest and the highest processing temperatures. However, large areas free from lead particles were observed in the specimen produced at the lowest mass temperature. At an intermediate processing temperature (190°C) which gave a maximum impact strength, the number of small lead-containing particles was at a minimum!

Paper VII

A simple method for estimating the level of gelation for rigid PVC pipes is the methylene chloride test. It consists of submerging the sample for 20 minutes in methylene chloride at 19°C . The severity of the surface attack caused by methylene chloride gives an indication of the level of gelation. This method cannot be used for pipes with a high level of gelation due to a poor attack by methylene chloride in this case. Another weakness of the test is that the severity of the attack is judged by visual inspection in a scale from 0 to 5, making it a rather subjective method.

A modification of the methylene chloride test has recently been introduced (42), according to which the attack of methylene chloride is determined at different test temperatures. An attack at 5°C indicates a lower level of gelation than an attack which first appears at 25°C. However, this and other modifications do not extend the applicability of the test to higher levels of gelation.

In the present work it was found that the attack by methylene chloride could be increased by electron irradiation of the sample prior to the methylene chloride test. This observation provided the basis for a method which extends the range of the methylene chloride test.

Proposed method

A sample of processed, rigid PVC, having a flat, smooth surface is prepared using a diamond saw. The sample is then inserted into a scanning electron microscope and a succession of several small areas (about 45x65 μm) are irradiated during equal times using successively higher beam currents. The sample is then submerged in methylene chloride at 19°C for 20 minutes, and is afterwards inspected using an optical microscope.

By observing the number of irradiated areas that have suffered a stronger attack by methylene chloride than the unirradiated surroundings, it is possible to find the lowest dose of irradiation that caused an increased attack. This dose is an inverse measure of the level

of gelation; i.e. the lower the dose, the higher the level of gelation.

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SEM studies of fractures of rigid PVC pipes

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Abstract

The fracture surfaces obtained in testing according to a standard method for time-to-failure under internal pressure were examined under a scanning electron microscope. The most frequent cause of fracture initiation at low pressures was found to be particles. Microanalyses by an energy-dispersive X-ray spectrometer indicated that the particles mainly consisted of impurities. The fracture surfaces obtained in tests at high stresses and short times were totally covered with threads and it was impossible to localize any point of initiation.

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1 Introduction

The use of plastic for pressure pipes has increased extremely rapidly in recent years because of its lower costs, easier handling and better corrosion resistance than competing materials. The viscoelastic behaviour of polymers presents a problem, however, as plastic pipes under pressure are prone to creep [1]. Long testing periods or well designed accelerated tests are required in order to estimate the ability of such pipes to withstand a certain pressure level for a reasonable service life. In the normal test procedure the time-to-failure under a constant internal pressure is measured at different stress levels. A prediction of the service life at a certain stress level is then usually attempted by extrapolation in a plot of log stress versus log time-to-failure [2]. The relationship between stress and time-to-failure is complicated, however. Extensive experiments have shown that different mechanisms lead to rupture at different stress levels [3–5]. At high stresses, which give short loading times, a brittle failure is commonly encountered. The probability of a ductile failure in this case increases with temperature. In an intermediate stress range, the failure is generally ductile. This region is in many cases followed by a second region of brittle fracture. The transition between ductile and brittle failure shows up as knees in the double logarithmic plots of stress versus time-to-failure [6,7].

The fracture surface can be considered to be a finger-print of the failure mechanism. It has previously been demonstrated that fractographic examinations of PVC might give information about the processes leading to rupture. The scanning electron microscope (SEM) makes it possible to study the microstructure of fracture surfaces [8] and to determine their compositions by simultaneous microanalysis [9]. The aim of this investigation was to study fracture surfaces obtained in normal testing of rigid PVC pressure pipes in order to see if a relation exists between long-term strength and fracture morphology.

2 Experimental

2.1 Material

A study was made of the fracture surfaces of 17 pipes of rigid PVC (110 × 5,3 PN 10) manufactured by Lubonyl AB, Sweden. The fracture surfaces were obtained from time-to-failure tests under constant internal pressure at 60 °C [10]. The samples chosen differed widely in time-to-failure (Table 1). All of the pipes were prepared from suspension PVC (Pevikon S 688, supplied by KemaNord, Sweden). Samples 1–16 were prepared from lead stabilized recipes, all of which were quite similar, differing only with respect to the amount of lubricants. These samples contained 1,6 % Pb and 0,4 % Ca. Sample 17 was tin stabilized and contained 0,3 % Sn, 0,2 % Ti and 0,8 % Ca.

2.2 Methods

The fracture surfaces were examined under a scanning electron microscope (JEOL JSM-U3) and by light microscopy. The SEM samples were sputter-coated with gold.

Analyses of the surfaces were carried out with an energy-dispersive spectrometer (PGT 1000) attached to the scanning electron microscope.

3 Results

3.1 Fracture topography

Fracture surfaces obtained in tests at low stresses had a topography quite different from those obtained at high stresses and short times. In the first case, the fractures seemed to have been initiated by particles of different kinds (Table 1). One example of this is shown in Fig. 1 (sample 4). This fracture surface contained a particle which consisted of resin that was not fully plasticized. The large grains consisted of small spherical particles of about $0,1\ \mu\text{m}$ in diameter. These were probably primary particles of E-PVC [11] present as an impurity. Cracks of different sizes could be seen within the emulsion particles (Fig. 1). These probably corresponded to the point where the fracture was initiated. This type of fracture, which has previously been called an adhesion fracture [12], was observed in 12 of the 17 samples studied. Another example is shown in Fig. 2 (sample 14). In this case the fracture surface contained a particle with a diameter of about $0,1\ \text{mm}$. As can be seen, a radial crackgrowth has occurred across the mirror area. At a high magnification (Fig. 3) the mirror area was found to be covered by fine threads. This indicated that the fracture was accompanied by plastic deformation. As also seen in Fig. 3, knots were present at the tips of the threads. These were probably formed by relaxation processes [13]. A comparison of different fracture surfaces showed that increasing time-to-failure tended to give finer threads and smaller knots, possibly due to a lower rate of crack propagation. The pattern of the fracture surface changed considerably beyond the mirror area (Fig. 2). Here, a similar rough structure could be seen as in fracture surfaces from impact tests [14], indicating a sudden increase in the rate of crack propagation. Similar transitions from a mirror surface to a rough fracture surface have previously been observed in PVC and in other polymeric materials [15, 16].

The pipes submitted to high internal pressure (17,7 MPa) were highly deformed by swelling and failed after a short time (Table 1). In these samples, the fracture surfaces were totally covered with threads (Fig. 4) and it was impossible to localize a point of initiation or a mirror area.

3.2 Fracture surface composition

In 12 samples the cracks seemed to have been initiated by particles. Analyses with an energy-dispersive spectrometer made it possible to divide these 12 samples into two groups. The first contained foreign particles, i.e. particles with a chemical composition different from that of the components in the recipe (Table 1) and the second particles which could be identified as unevenly dispersed additives. Sample 15 is representative of the first group. Here, a bluish-green particle was observed in the fracture surface by optical microscopy. According to SEM studies it consisted of small crystals (Fig. 5).

Table 1. Appearance and distribution of elements in the fracture surfaces.

Sample	Recipe	Stress (MPa)	Time-to-Fracture failure initiation (h)	Na	Mg	Al	Si	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Pb
1	A1	13,7	1018			+	+	+	+	+	+	+	+	+	+		+
2	A1	15,7	376			+	+	+		+	+			+			+
3	A2	12,3	173	+	+	+	+	+									+
4	A3	15,7	231			+	+	+	+	+				+			+
5	A4	13,7	79					+		+							+
6	A4	15,7	549			+	+	+		+				+			+
7	A5	15,7	907			+	+	+	+	+	+	+	+	+	+		+
8	A6	13,7	294			+	+	+		+	+			+			+
9	A6	15,7	597			+	+	+		+							+
10	A7	13,7	329			+	+	+		+							+
11	A7	15,7	187			+		+		+		+		+			+
12	A7	17,7	31					+		+							+
13	A8	12,3	255			+	+	+		+				+			+
14	A8	13,7	336			+	+	+	+	+	+	+	+	+	+		+
15	A8	15,7	525					+		+						+	+
16	A8	17,7	38			+	+	+		+				+			+
17	B1	12,3	2309			+	+	+		+	+			+			+

○ = Elements present in the particles initiating the fracture

□ = Elements present in the particles originating from the testing equipment

Microanalysis gave the spectrum in Fig. 6, indicating the presence of gold (deposited during coating), chlorine and copper. The observations thus indicated that the particle might consist of copper chloride. However, a comparison with a pure copper chloride standard gave a $\text{Cl-K}\alpha$ peak with a higher relative intensity than the sample. A tentative explanation might be that the particle originally consisted of copper, which, during testing, reacted with evolved hydrochloric acid and water and thus became verdigrised.

In sample 11, the particle consisted of twisted threads with a diameter of $3\text{--}5\text{ }\mu\text{m}$ (Fig. 7). According to microanalysis, these could be filings from the extruder mixed with additives.

The central part of the fracture surface of sample 17 (Fig. 8) had a yellow colour due to dehydrochlorination. In the corresponding part of the fracture surface, the X-ray dot image (Fig. 9) showed a local concentration of calcium. An uneven distribution of additives might have caused the initiation of the fracture, since no foreign particles could be detected.

4 Discussion

As PVC is a heterogeneous material, many defects can be present in the pipe. Every fault acts as a stress concentrator and may initiate a fracture. In the present study the most frequent cause of fracture initiation was found to be foreign particles (Table 1). In some cases, however, particles were also observed which obviously had nothing to do with fracture initiation. Without exception they all contained a high concentration of alumina (Table 1) and were in loose contact with the matrix. This was evident from the charge-up phenomena which they demonstrated. These particles probably originated from the testing equipment. It is very unlikely that deposited particles of this type can become pressed into the fracture surface after the test and be mistaken for an impurity in the pipe.

No rational explanation for the relatively short time-to-failure of sample 5 could be obtained by scanning electron microscopy. The possibility that fracture initiation was caused by incomplete gelation of the S-PVC particles was considered. In a study carried out by HASSANDER and TÖRNELL [17] sample 5 was embedded in a mixture of methyl and butyl methacrylate, and ultrathin sections [18] were then studied by transmission electron microscopy. The sample taken from the fracture surface was found to contain particles of the same size as the primary particles found in S-PVC, whereas a sample taken far away from the fracture surface did not show the presence of such large PVC particles. This suggests that inhomogeneous gelatinization may also be a source of failure in moulded rigid PVC.

Samples 12 and 16 were obtained in tests at a high internal pressure, which produced failure within a rather short time. The fracture was preceded by severe swelling, and resulted in a fracture topography quite different from the other samples.

The topography of the fracture surface studied in this work illustrates that several different failure mechanisms are operative in PVC pressure pipes. This indicates the difficulties which exist in designing accelerated tests and emphasized the difficulties in estimating the service life by extrapolations from long-term strength data.



Figure 1. Cracks within an E-PVC particle. Primary particles, size about 0,1 μm (sample 4).

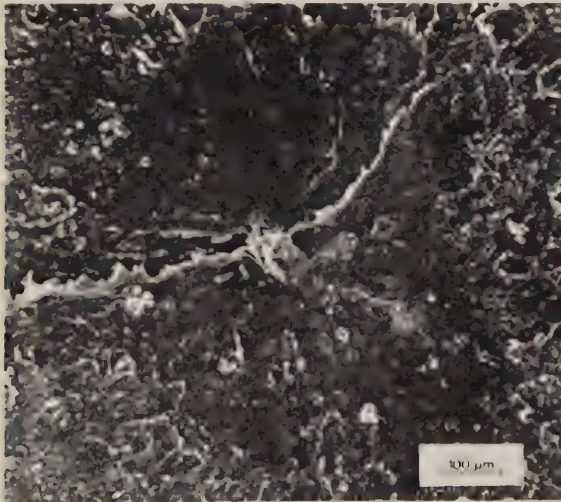


Figure 2. A foreign particle in the central part of the mirror area (sample 14). A radial crack-growth has occurred across the mirror area. A transition to a rough surface can also be seen.

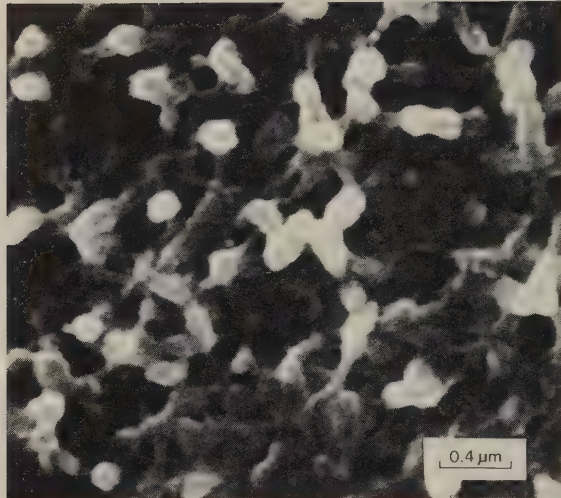


Figure 3. Knots at the tips of the PVC threads in the mirror area of sample 14.

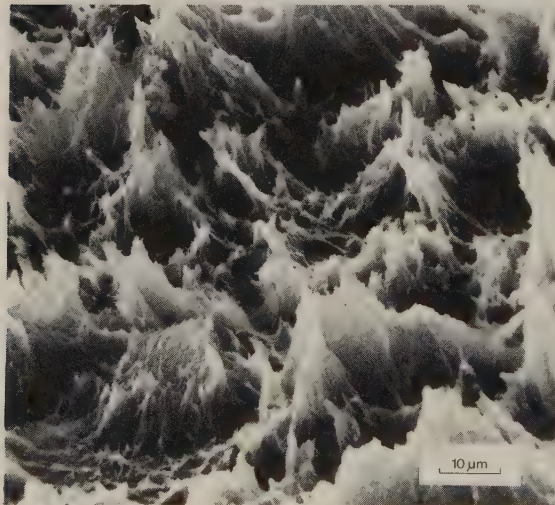


Figure 4. The rough fracture surface of a pipe submitted to high internal pressure (sample 12).



Figure 5. A particle consisting of small crystals initiating the fracture in sample 15.

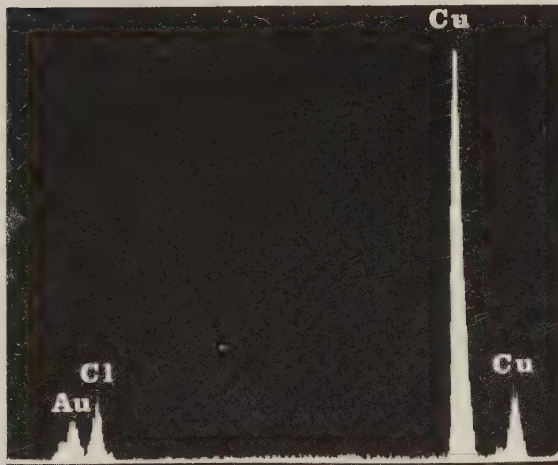


Figure 6. Spectrum of the crystals shown in Fig. 5.



Figure 7. A particle consisting of twisted threads in the fracture surface of sample 11.



Figure 8. Topography image of the point of initiating of the fracture in sample 18.

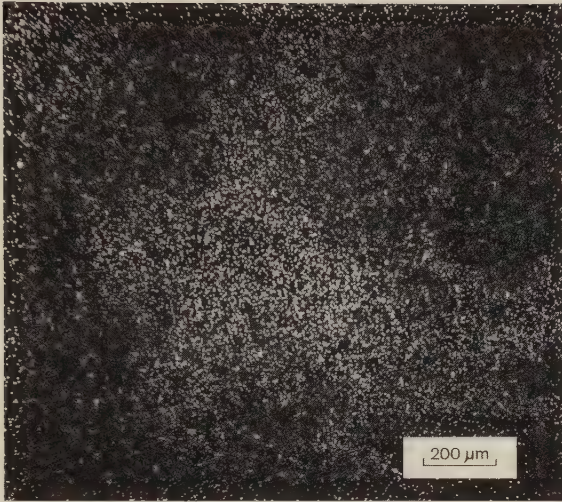


Figure 9. Ca-K α X-ray image corresponding to Fig. 8.

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II

Ch 150

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P O L Y T E C H N I C A

S C A N D I N A V I C A

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The effect of processing conditions and resin structure
on impact strength; long-term performance and fracture
morphology of rigid PVC pipes

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ABSTRACT

Rigid PVC pipes were prepared from four commercial suspension PVC resins of equal K-values, using four different double screw extruders. For each resin-extruder combination a set of compounds with different lubricant contents was run in order to vary the level of gelation. The experiments were carried out in order to study the possible effect of resin structure and processing conditions on the quality of the pipes.

The falling weight impact strength of the pipes was found to depend on the choice of resin. An increase in the amount of lubricant resulted in a decrease in the resistance to internal pressure.

The fractographic investigation by light and scanning electron microscopy revealed that the large variation observed in the time-to-failure was partly a result of the different modes of failure. In the present study, the main cause of fracture initiation seemed to be the presence of pigment agglomerates within the pipe wall. In some cases the fracture occurred via semi-elliptical surface cracks, indicating that the fracture was probably initiated by notches or by regions of bad gelation.

1 INTRODUCTION

The properties of rigid PVC pipes are thought to be affected by many different factors, such as resin morphology, the formulation of the compound, and processing conditions. In this work pipes prepared from four commercial suspension PVC resins of equal K-values were compared in order to elucidate the possible effect of resin structure on product quality. Four double screw extruders with different capacities were used in order to permit the elucidation of resin and machine factors.

In general, the results with most PVC processors seem to indicate that high strength with long loading times normally requires a more complete gelatinization than that which gives maximum impact strength. In order to characterize the pipes, therefore, both impact and long-term burst strength were studied. Studies of this type are rather time consuming and expensive. It would therefore be of great value to find a screening test which might give a rough indication of pipe quality. One test of this kind would be the methylene chloride test, which was also used.

Some fracture surfaces were investigated under the light microscope and by scanning electron microscopy in the hope of discerning the processes responsible for fracture initiation.

2 MATERIAL AND METHODS

2.1 Resins

Table 1 gives the properties of the four resins used in the tests. All of these resins are intended for use in pipe production. Two of the resins had a relatively high porosity (Pevikon S 688 and resin A), the others being rather compact (Pevikon S 684 and resin B). One of the porous resins, Pevikon S 688, was skinless. All the experiments with a

Table 1 Resin properties

Resin	Pevikon S 688	Pevikon S 684	Resin A	Resin B
K-value	68.0	67.5	69.5	69.0
Bulk density (kg/l)	560	600	540	560
Porosity ^{x)} (%)	23	18 ^{xx)}	27	20
Particle size distribution				
> 250 μm	0.8	0.4	1.0	3.2
< 100 μm	0.2	1.0	3.2	6.8
Mean value (μm)	180	150	162	152

x) Mercury intrusion porosimetry

xx) 25% porosity for Pevikon S 684 b

particular resin were carried out using resin from the same batch.

2.2 Extruders

Four extruders with different capacities were used (Table 2). They were all of the twin-screw type and had provisions for screw temperature regulation.

2.3 Formulations

Except for the amount of lubricant, the same basic formulation was used in all of the experiments (Table 3). The pipes obtained from the Cincinnati CM 80-extruder were pigmented (Table 4), the others not. For each combination of resin and extruder, a set of formulations differing in the amount of lubricant was used in order to cover a fairly wide range in the degree of gelation. The range within which the amount of lubricant was varied was chosen partly on the basis of

Table 2. Extruders

Extruder	Screws (mm)	Screw speed (rpm)	Peripheral speed of the screw (m/s)	Capacity (kg/h)
Weber DS 45	D=2x45 L=17xD	60	0.14	50
Cincinnati CM 2/80	D=2x80 L=18xD	26	0.11	180
Cincinnati CM 80	D=2 (80-130) L=1655	27	0.11-0.18	400
Krauss Maffei KMD 90	D=2x90 L=21xD	27	0.13	260

previous experience of acceptable processing conditions (back-pressure, energy consumption, output, and mass temperature) for the various resins and partly on the results of trial runs on the effect of lubrication on impact strength. All the formulations were weighed in at the KemaNord AB laboratories, Sweden.

Table 3. Basic formulation

PVC	100
Tribasic lead sulfate	1.5
Dibasic lead sulfate	0.5
Stearic acid	0.3 (0.2 for Weber DS 45)
Calcium stearate	0.4
Calcium carbonate (FF Special)	1.0
Paraffin wax, mp 100°C	0.08-0.62
Pigment 42-1173-002	0.2 (only for Cincinnati CM 80)

Table 4. The composition of pigment 42-1173-002

Component	Color
PbCrO_4	yellow
PbMoO_4	red
Carbon black	black
BaSO_4	white

2.4 Falling weight impact strength (B_{50})

The pipes were tested at a temperature of 0°C with a falling weight of 2 or 3 kg, depending on the pressure class of the pipes. The falling weight impact strength (B_{50}) was taken as the height at which 50% of the pipes failed. The equipment allowed falling heights up to 450 cm.

2.5 Internal pressure resistance

The resistance to internal pressure was determined as the bursting time at 60°C and at different stresses. Two samples were run in each testing condition. The time-to-failure for the first of the samples was taken as the bursting time.

2.6 Methylene chloride tests

The pipe sections were submerged in a bath of methylene chloride at 20°C for 30 minutes. The surface attack on the pipes was judged according to a subjective scale from 1-5, where 1 indicated no attack.

2.7 Microscopy methods

Ultra-thin sections of the resins were examined by transmission electron microscopy (Zeiss EM-19). The specimens were embedded in a mixture of 70 parts methyl methacrylate, 30 parts butyl methacrylate and 4 parts 2,4-dichlorobenzoyl

peroxide. The fracture surfaces were examined by light and scanning electron microscopy (ISI 100 A). The SEM samples were sputter coated with gold/palladium and carbon. Analyses of the surfaces were carried out with an energy dispersive X-ray spectrometer (PGT 1000) attached to the scanning electron microscope.

2.8 Statistical methods

The Spearman two-tailed rank correlation test corrected for ties was used to assert the significance of the results [1].

3 RESULTS

3.1 Structure of the resin

The internal structure of the four suspension resins is illustrated in Figs. 1-4. Pevikon S 688 and resin A appear to have a more homogeneous texture than Pevikon S 684 and resin B. Pevikon S 684 in particular had a coarse and compact texture and a relatively low porosity (Table 1).

3.2 Impact strength (B_{50})

The falling weight impact strength (B_{50}) varied with the resin quality and with the amount of lubricant (Figs. 5-8). An attempt to rank the resins according to maximum impact strength gives Pevikon S 688 > resin A > Pevikon S 684 > resin B. This ranking was the same irrespective of the extruder used. Resin A was only tested in two extruders. The results indicate that a porous and skinless resin may give a higher impact strength than a compact resin with skin. This conclusion is also in agreement with results obtained by comparing the normal Pevikon S 684 with a modified type (S 684 b) with a higher porosity (25% as compared with 18%) (Fig. 6).



Figure 1. Pevikon S 688

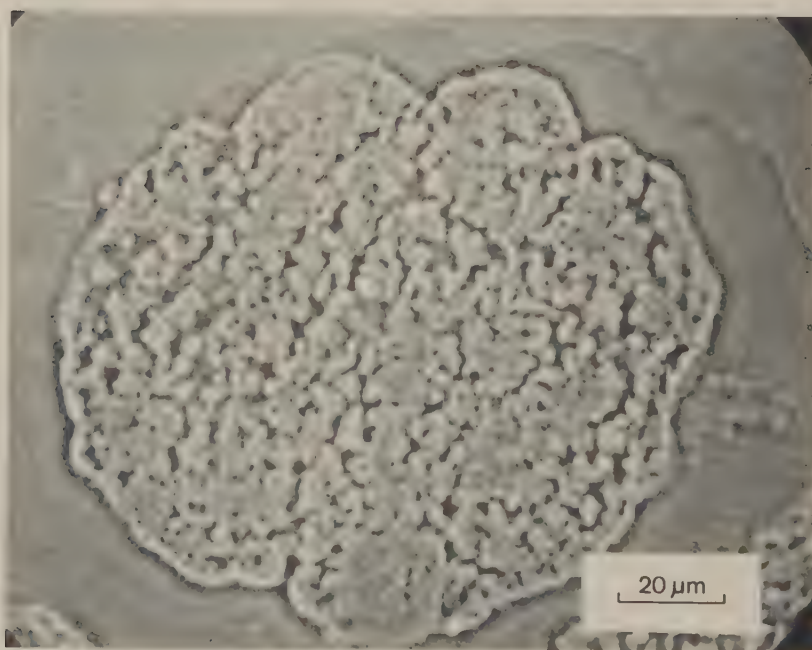


Figure 2. Pevikon S 684

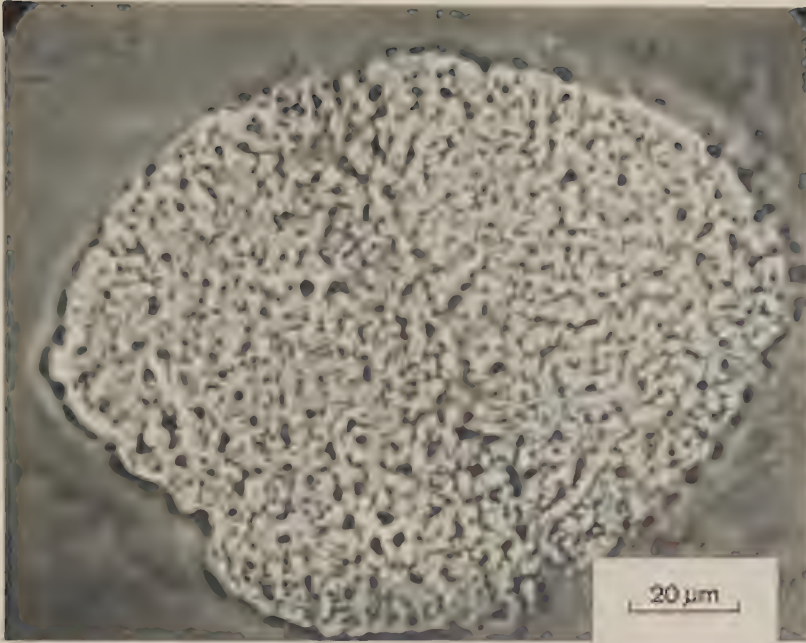


Figure 1. Resin A

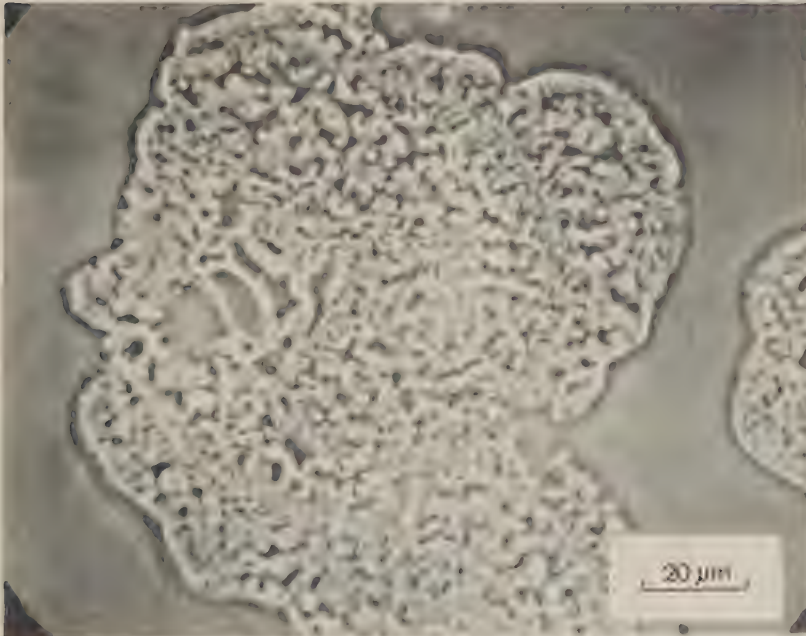


Figure 4. Resin B

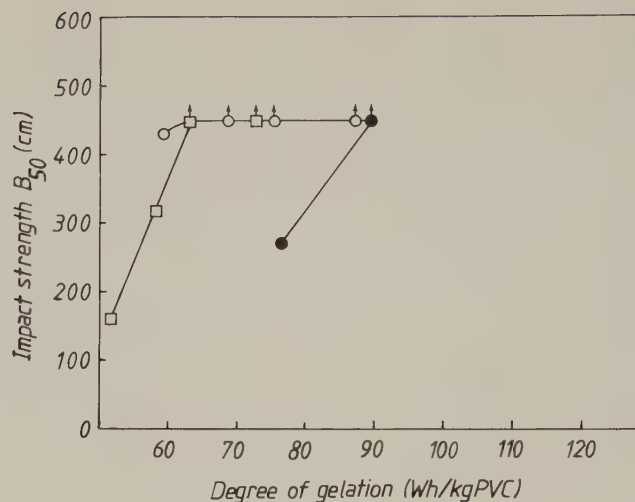


Figure 5. Effect of gelation on impact strength measured as B_{50} .
 Extruder: Cincinnatti CM 80
 Pipe dim.: 110 NT6
 Falling weight: 3 kg
 Temp.: 0°C

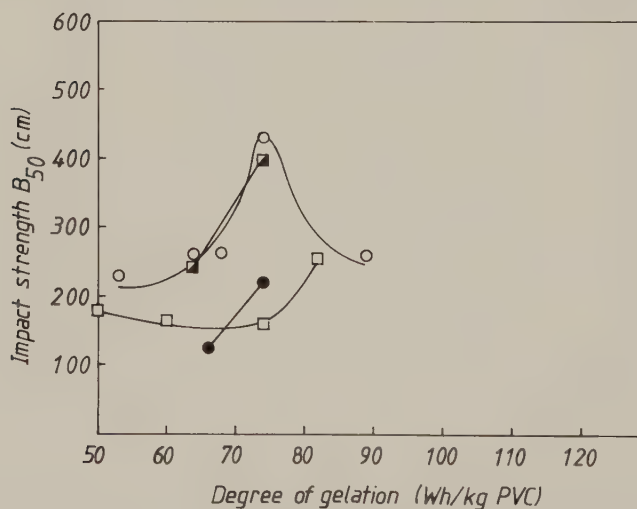


Figure 6. Effect of gelation on impact strength measured as B_{50} .
 Extruder: Krauss Maffei KMD 90
 Pipe dim.: 90 NT10
 Falling weight: 2 kg
 Temp.: 0°C

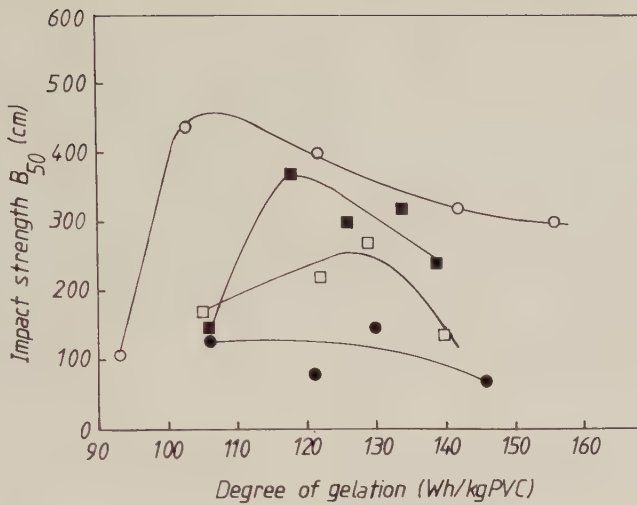


Figure 7. Effect of gelation on impact strength measured as B_{50} .
 Extruder: Weber DS 45
 Pipe dim.: 50 NT10
 Falling weight: 2 kg
 Temp.: 0°C

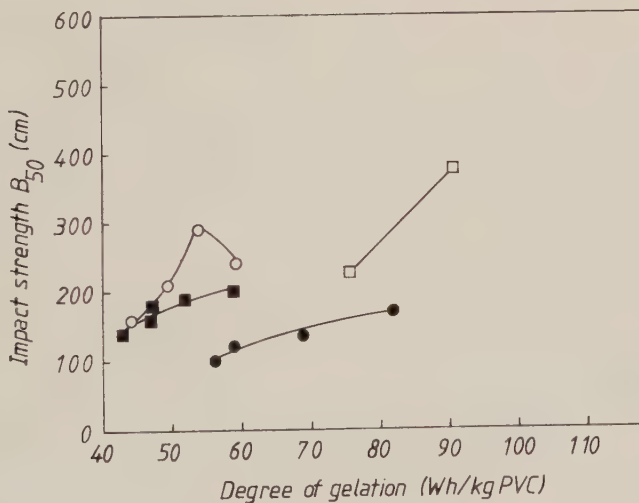


Figure 8. Effect of gelation on impact strength measured as B_{50} .
 Extruder: Cincinnati CM 2/80
 Pipe dim.: 90 NT10
 Falling weight: 3 kg
 Temp.: 0°C

3.3 Resistance to internal pressure

It seems that the ability of the pipes to resist internal pressure over a long period of time increases with an increase in the level of gelation or a decrease in the amount of lubricant (Figs. 9-10). Because of the rather limited size of the experimental material and the fairly broad scatter in the time-to-failure data no conclusions could be drawn about the effect of resin structure on the long-time behavior of the resulting pipes.

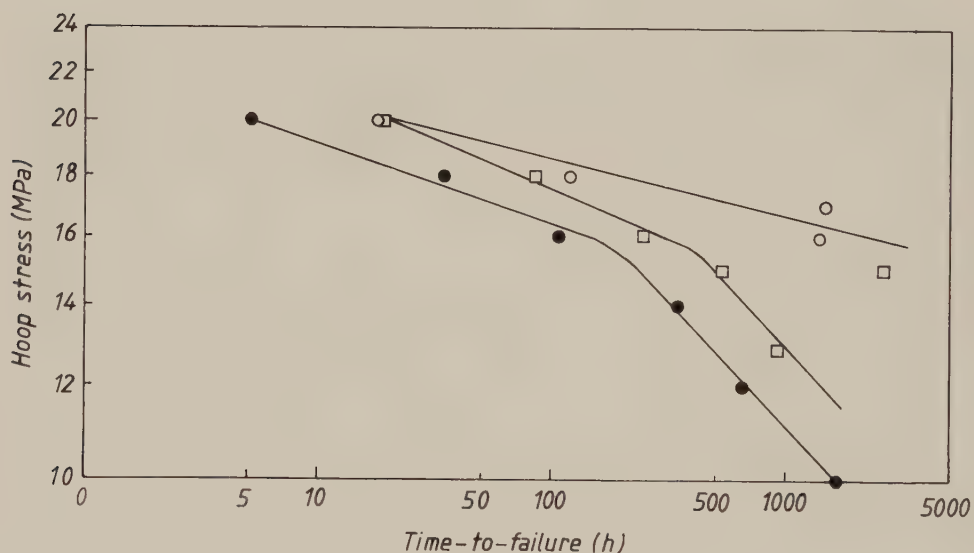


Figure 9. Effect of gelation level on resistance to internal water pressure at 60°C.

Extruder: Cincinnatti CM 80

Resin: Pevikon S 684

○ Amount of paraffin wax: 0.26 phr PVC
□ " " : 0.36 " "
● " " : 0.62 " "

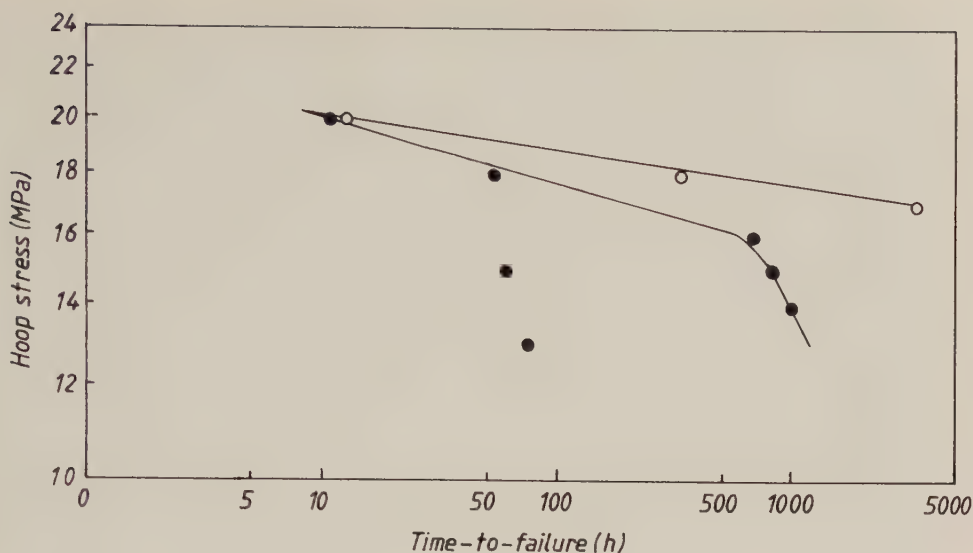


Figure 10. Effect of gelation level on resistance to internal water pressure at 60°C.

Extruder: Cincinnatti CM80

Resin: Pevikon S 688

○ Amount of paraffin wax: 0.26 phr PVC

● " " : 0.62 " "

3.4 Methylene chloride tests

An increase in the amount of lubricant adversely affected gelation as determined by the methylene chloride test ($r_s = 0.803$, $p < 0.01$, corrected for ties) (Table 5).

3.5 Fractographic studies

The fracture surfaces indicated different modes of failure (Fig. 11). In a number of cases the fracture surfaces contained inclusions with different sizes.

Table 5. The methylene chloride test

<u>Weber DS 45</u>	<u>Amount of lubricant</u>						
	0.08	0.12	0.18	0.26	0.36	0.48	0.62
Pevikon S 688		1	1	1	1	1.8	
Pevikon S 684	1	1	1	1			
Resin A	1	1	1	1	1.8		
Resin B	1	1	1	1.2			
 <u>Cincinnati</u> <u>CM2/80</u>							
Pevikon S 688				1	1.4	1.4	2.2
Pevikon S 684		1	1				
Resin A		1	1	1.4	1.4	2.2	2.6
Resin B		1	1.4	1.4	2.2		
 <u>Cincinnati</u> <u>CM 80</u>							
Pevikon S 688				1	1.4	1.8	2.8
Pevikon S 684				1.6	2.8	3.4	3.8
Resin B			1	1.2			
 <u>Krauss Maffei</u> <u>KMD 90</u>							
Pevikon S 688			1	1	1.4	2.2	
Pevikon S 684		1	1	1.4	1.4		
Resin B			1	1			
Pevikon S 684 b			1	1			



Figure 11 a. An inclusion in the central part of a PVC pipe's fracture surface. The direction of fracture propagation is shown by the arrows.

Fig. 11 a exemplifies a fracture surface of this type. The light microscope showed these inclusions to be red and yellow and most of them had a particle size between 50 and 100 μm . They were found in the pigmented pipes and, according to energy dispersive X-ray analysis, contained chromium and lead as the only detectable foreign elements (Fig. 12). This indicated that they consisted of agglomerates of the red and yellow components of the pigment used. The pigment agglomerates were cracked, which must have happened during testing and not during preparation for microscopy. One proof of this was the fact that the fractured surfaces of the pigment agglomerates were contaminated by depositions from the pressure water of the pipe testing system. More evidence was obtained by analysis of an X-ray exposure of a tested pipe which contained more than one hundred growing cracks. The X-ray film showed that the particles in the cracks were fractured. All the growing cracks in this pipe were studied

by light microscopy and about 10 by electron microscopy. It was found that, in general, fragments of pigment particles were attached to both of the fractured surfaces. This study also showed that the largest pigment agglomerates were present in the two cracks which had penetrated the pipe wall and caused the actual failure.

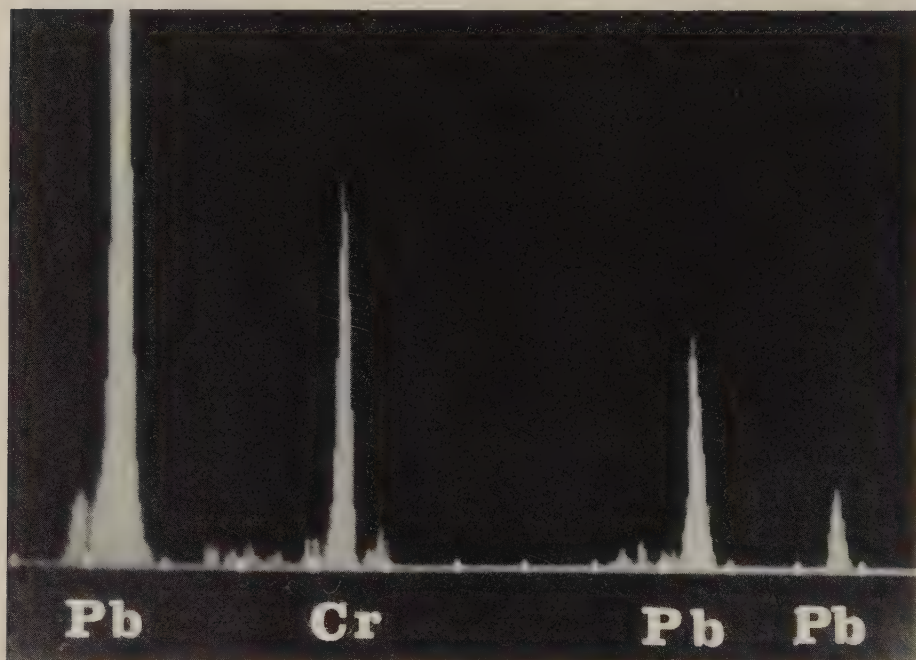


Figure 12. X-ray spectrum of pigment agglomerates in the fracture surface of a PVC pipe.

Particles containing lead as the only detectable element were found in the fracture surfaces of both pigmented and unpigmented pipes. These particles were very small, 1-20 μm , and probably originated from the stabilizer (Fig. 13). Foreign particles of uncertain origin were also found.

The fracture surfaces which contained inclusions indicated that polymer fracture was initiated at the particle/matrix interface. The smooth mirror area that can be seen around the particle was created during crack propagation (Fig. 11 a). The circular boundary gives the position at which the sub-critical propagation terminated and the crack propagation

began to accelerate [2]. An analysis of 27 fracture surfaces showed that the size of the mirror area increased with the thickness of the pipe wall as measured after the test ($r_s = 0.518$, $p < 0.01$ corrected for ties).

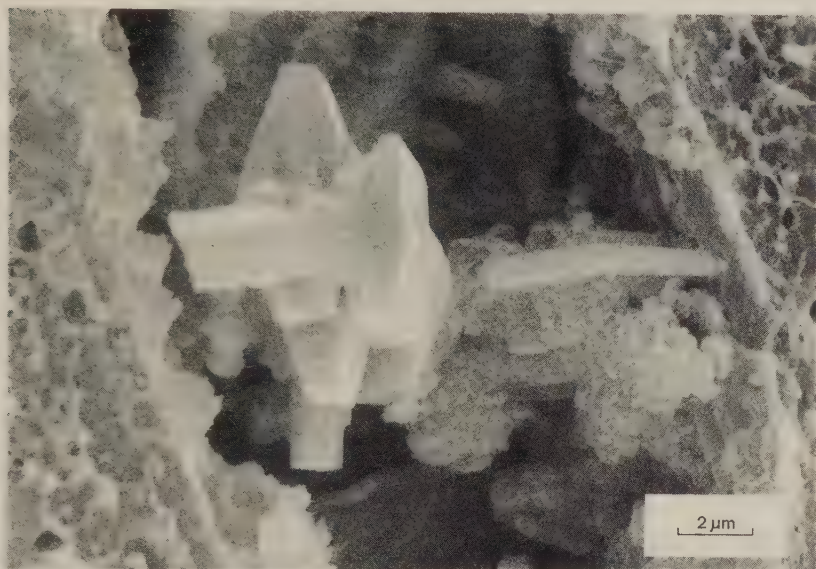


Figure 13. An inclusion containing lead in the central part of a PVC pipe fracture surface.

The type of fracture exemplified by Fig. 11 b can be characterized as a semi-elliptical surface crack. In these cases no particles were found in the fracture surfaces, indicating that the fracture was initiated by notches or by regions of bad gelatinization.

Only one example of the fracture mode illustrated in Fig. 11 c was found. Previous experience indicates that this type of fracture is probably more frequent at higher pressure levels. It can be characterized by the total absence of a planar surface. The fracture in this case was initiated in the central part of the pipe wall. There was no sign of inclusions or of any area indicating subcritical crack propagation.

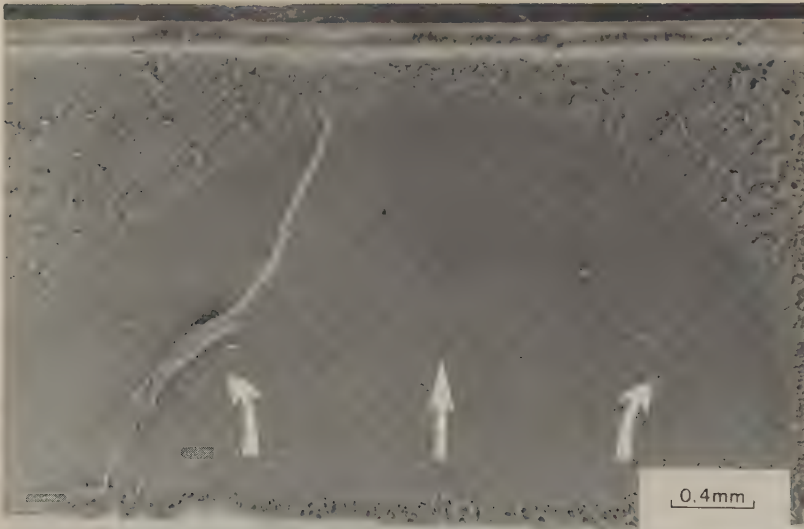


Figure 11 b. A semi-elliptical surface crack in a fracture surface of a PVC pipe. The direction of fracture propagation is shown by the arrows.

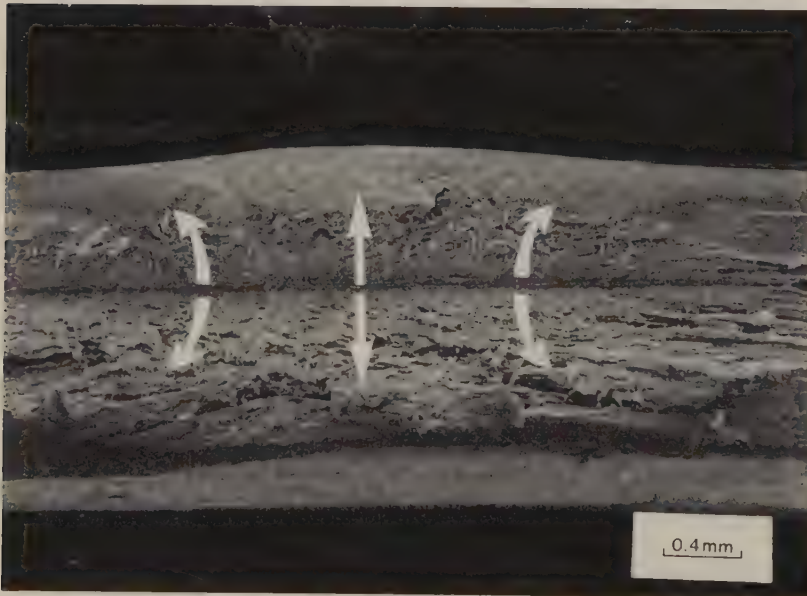


Figure 11 c. A PVC pipe fracture surface without an area of subcritical crack propagation. The direction of fracture propagation is shown by the arrows.

3.6 Discussion

The different resins gave pipes which differed greatly in impact strength. This can probably be referred to differences in the internal structure of the resins. Some of these differences may remain unchanged during processing and affect the energy absorption of the processed material under impact conditions. Pipes from Pevikon S 688 showed a high impact strength (>450 cm) over a wide range of lubrication. This may be important, as it implies that the impact strength of the product would be rather insensitive to fluctuations in the processing conditions. The reason might be that Pevikon S 688 is skinless and has a narrow particle size distribution [3]. However, the effect of varying the amount of lubricant was different with the four extruders. This shows that it is difficult to design experiments which can be used to compare the quality of different resins without choice of formulation or extruder being influential.

BOLLMAN and DETTKE [4] have shown that the resistance of PVC pipes to internal pressure increases with rise in K-value. The present experimental data do not permit conclusions to be drawn about the presence of a resin structure effect. One reason is that most of the data were obtained in experiments with pigmented pipes, in which the time-to-failure was influenced not only by the polymer but also by the presence of pigment agglomerates. In fact, the presence of pigment agglomerates was the main reason for fracture initiation in this study. This demonstrates the need for great caution in the choice of pigment compounds and other additives which may aggregate.

The pigment agglomerates seemed to be rather active as fracture initiators. In agreement with the findings made in this study, this behavior can probably be explained by their low internal strength. In the pressurized pipes the pigment agglomerates broke under the influence of tensile forces exerted by the strained matrix. This would result in the rapid formation of thin, extended cracks, comparable to the

size of the agglomerates. In this way inclusions of low strength, nondeformable materials would act as very effective fracture initiators. Such materials might even be used on purpose to facilitate studies of crack propagation.

The results reproduced in Figs. 9-10 showed that a high level of lubrication resulted in a decrease in the time-to-failure. The methylene chloride test showed that this was due to bad gelation. This would suggest that a large scatter in the time-to-failure data might well be due to a nonhomogeneous distribution of the lubricant between and within the individual particles of the formulated resin. Accordingly, the porous structure and its accessibility to the lubricants and other processing aids during mixing would, together with the particle size distribution, perhaps be the most important resin properties in determining the practical long-time behavior of the finished pipes. A comparison between different resins in these respects would require a comparison between the short-time branches of the time-to-failure distributions obtained with the different resins at a relevant stress level. Such a comparison would be very time consuming and expensive.

The curves in Figs. 9-10 seem to change slope at high levels of lubrication. Such a change in slope has previously been identified as a transition from a ductile to a brittle failure. It has also been suggested that the point of transition is determined by the amount of lubricant [5]. Accordingly, the results in Fig. 10 would suggest that with a large amount of paraffin wax this transition occurred at around 50 or 700 hrs. An inspection of the fractured pipes showed that the two pipes that failed between 50-100 hrs at low stress did so after having been severely deformed by an uneven, local expansion, during which the wall thickness had been reduced to almost half its original size. The reason might be an increased rate of deformation at the thinnest part of the pipe. The two pipes that failed around 1000 hrs (Fig. 10), however, showed the characteristics of brittle failure. It is thus likely that the "knee" in the lower curve in Fig. 10

marks the onset of brittle failure.

Fig. 9 shows that two pipes in the series with 0.36 phr PVC paraffin wax failed after 538 h and 2641 h at 15 MPa. The fracture investigation revealed two different fracture modes. In the first case (538 h) the failure was due to a surface crack (Fig. 11 b) probably initiated at a severe notch created during processing. A reduction in time-to-failure due to notches has previously been reported in the literature [6,7]. In the second case (2641 h) the failure was initiated at a pigment agglomerate within the pipe wall. In this case the large difference in time-to-failure could be referred to differences in fracture mechanism. It should be pointed out, however, that small temperature and pressure variations in the testing system may also introduce variations in time-to-failure [8].

The results discussed show that fractographic studies may give an understanding of the fracture mechanism and provide information of importance for the formulation of resin compounds and the evaluation of tests to predict the service life of pressure pipes.

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III

The scattering in time-to-failure for rigid PVC pipes
produced from a particle-free formulation.

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ABSTRACT

Rigid PVC pipes prepared from a particle-free formulation were subjected to a constant internal pressure test (16 MPa, 60°C) in order to study the scattering in time-to-failure. Scanning electron microscopy of the fracture surfaces indicated that different fracture mechanisms were operative.

Despite the fact that efforts were made to produce pipes free from foreign particles, most failures were initiated by particles. These were soft and rubber-elastic. Besides the cracks that led to failure, several growing cracks were observed. The results suggest that a soft particle represents a serious flaw and that fracture initiation occurs earlier the larger the particle is. A comparison of fracture surfaces showed that an increase in the time-to-failure was accompanied by an increase in the size of the mirror area and a less pronounced creep-thinning of the pipe wall. These effects, which point to a transition towards a more brittle failure with time, was probably caused by physical aging of the pipe material during the test period.

INTRODUCTION

Previous investigations of rigid PVC pipes submitted to internal pressure tests have indicated that the time-to-failure distribution is fairly broad. Most failures are initiated by particles. These may be pigment agglomerates (1), filler particles or solid impurities (2,3). The present study was confined to PVC pipes prepared from a particle-free formulation. The original aim was to study the scattering in time-to-failure when fracture initiation by particles was excluded. The pipes were tested at constant hoop stress and the reasons for fracture initiation at different bursting times was investigated by scanning electron microscopy.

EXPERIMENTAL

The pipes (110 X 5.3 PN 10) were produced from a skinless suspension resin, Pevikon S 688 (KemaNord) using a soluble, tin-based stabilizer (Tab.1). No fillers or pigments were added in order to keep the number of particles as small as possible. The pipes were produced on a Krauss Maffei KMD 90 extruder in the laboratories of Lubonyl AB (presently Uponor AB).

The bursting time at a constant hoop stress of 16 MPa was determined at 60°C according to ISO 1167. The time-to-failure was taken as the bursting time for the first failure of two pipes, each with a length of 480 mm, tested in parallel. In total, nine pairs of pipes were tested. Of each pair, the pipe that burst was subjected to fractographic studies; the other was discarded.

The areas of the pipes that contained shear bands were sawn out. The cracks were uncovered by breaking the samples after cooling to liquid nitrogen temperature. Two types of cracks could be distinguished; growing cracks and cracks penetrating the wall. These were separated by the presence of depositions from the pressure water on the fractured surfaces of the penetrating cracks.

The fracture surfaces were examined by using a light microscope and a scanning electron microscope (ISI 100A). The SEM-samples were covered with gold/palladium by sputtering.

Qualitative analyses of the surfaces were carried out with an energy dispersive X-ray spectrometer (PGT 1000) attached to the scanning electron microscope. In this case, carbon-covered samples were used.

The Spearman two-tailed rank correlation test corrected for ties was used to assert the significance of the results (4).

RESULTS

A broad distribution in the time-to-failure was obtained (Tab.2). Growing cracks were found in five of the nine pipes. The nature of the nine fracture surfaces and the position in the pipe wall of the points of fracture initiation are indicated in Fig.1. Unexpectedly, the fractographic studies revealed that, in six of the pipes the failure was initiated at a particle/matrix interface despite the fact that a particle-free formulation was chosen.

An example of a fracture surface containing a particle is shown in Fig.2. Particles were also found in all of the growing cracks. In the pipes that contained growing cracks, the largest particle was found in the crack that caused the actual failure. Among the fractures initiated by particles positioned in the interior of the pipe wall, there seems to be a trend towards shorter times-to-failure at increasing particle size (Fig.1). This trend is in accordance with previous results (1).

All of the particles observed were found to be rubber-elastic. They were easy to remove from the fracture surfaces and may be regarded as cavities in the PVC-matrix. The particles contained sulphur, chlorine, calcium, titanium and zinc according to energy dispersive X-ray analyses (Fig.3). A quantitative analysis of an isolated particle using particle induced X-ray emission (PIXE) (5) gave the results shown in Table 3. Not even the quantitative composition data provided by the PIXE method gave a clear indication as to the origin of the particles.

Around the particles mirror areas were formed. The size of the mirror area increased with the time-to-failure (Fig.4) ($r_s = 0.656$, $p < 0.01$, corrected for ties). It was also found that the filamentary structure of the mirror area changed from a rough to a smooth texture with increasing time-to-failure (Fig. 5). In a given pipe, the filaments in the mirror area were found to be smaller in growing cracks than in the crack that caused the failure (Fig.6). Throughout a given mirror area, the structure was rather

uniform. Ripples spreading radially from the particle (as seen e.g. in Fig.2) were found in several cases, especially if the particle was large. This indicates that the crack has propagated in slightly different planes.

With two of the pipes (samples 2 and 4), the fracture was initiated near the interior wall. Both of these failed relatively early. In sample 2, the fracture was initiated by a particle, whereas the fracture of sample 4 was initiated by another type of flaw. The experimental material is too sparse to permit conclusions. However, the rather short time-to-failure observed with these samples is in agreement with a previous observation that a surface crack may result in a short time-to-failure (1).

In the fracture surface of sample 1 (the shortest time-to-failure), neither particles nor an area for subcritical crack propagation were found. In this case, the failure was caused by a slanting crack which formed a 12 degree angle to the axial direction. The other pipes contained axial cracks only. This is the expected situation as the hoop stress is the maximum stress. The orientation of the PVC-molecules would also favour axial crack formation.

The fracture surface of sample 9 (the longest time-to-failure) contained no particles. It was planar with a large (3×0.15 mm) line defect (Fig.7).

At the external and internal pipe walls, shear bands were observed at all the fractures. Data giving the wall thickness

at the point of fracture initiation for all of the nine pipes have been included in Tab.2. It is obvious that the types of failure studied in this work are associated with yielding and an extensive local creep. Similar results have been reported by Kirstein from measurements on cracks initiated by notches (2). For the particle induced cracks, it is clear that the extent of wall thinning at the point of fracture initiation decreases with an increase in the time-to-failure ($r_s = 0.782$, $p < 0.01$, $N = 14$, corrected for ties). This can be expressed as a change to a more brittle failure at long bursting times.

DISCUSSION

The knowledge of the subcritical crack speed is essential for a correct evaluation of the fracture mechanism. For PMMA, this speed has been reported to vary between 6-21 cm/s (6), which means that in this material the mirror area would be created very rapidly. The corresponding data for PVC as reported from studies using an undisclosed technique indicate that the mirror area starts to grow at about 90 % of the pipe's lifetime (7). Gaube et al. (8) have reported that the cracks appear shortly before the final failure. This would indicate that the cracks grow at considerable rates once they are initiated (9). It has also been stated that if the rate of propagation is fast, the pipe will contain only one crack when the failure occurs (10). According to Niklas and Kausch, this seems to be the normal situation with rigid PVC-pipes (11). In a study of 250 pipes, they found only a few growing cracks, and concluded

that crack propagation does not contribute to the lifetime of the pipes.

In this investigation, many growing cracks were found (Tab.2). This might be explained by the presence of relatively large rubber-elastic particles with a modulus considerable lower than that of the matrix. The observation in this work of several growing cracks is not unique. In a previous study, in which fracture initiation occurred by pigment agglomerates, i.e. by particles having a very low cohesive strength, a pipe was found which contained about 100 growing cracks (1). The results strongly indicate that soft particles or particles with a low cohesive strength represent very serious flaws. The fact that a pipe can contain growing cracks of different sizes indicates that, at least under the conditions normally used in pressure testing of PVC-pipes, the time necessary for a growing crack to reach its critical size is not negligible in comparison with the time-to-failure. Before a more quantitative statement can be made, it seems necessary to perform direct measurements of the crack growth rate under different conditions.

It might be argued that the structure of the mirror area would give some information about the crack growth rate. The fine structure obtained at long times-to-failure, would thus indicate a lower rate of propagation than would the rough mirror area found in pipes which failed at shorter times. However, great caution is needed in using the fracture surface appearance as a base for esti-

mating crack speed rates, as the pipes are subjected to aging during testing. The test is carried out during a long period of time at a fairly high temperature (60°C). Aging at this temperature is known to strongly affect the mechanical properties of rigid PVC (12). The finer structure of the mirror area observed at a longer time-to-failure may thus very well be a result of the more extensive physical aging or annealing that would have occurred in this case before the instant of fracture initiation. This explanation is in agreement with the observation that in the pipes containing growing cracks, the roughest mirror area was found around the largest particle, i.e. in the crack that caused the failure and hence, most probably started to grow first. This discussion of the role of physical aging presupposes that fracture initiation occurs rather late during the test period.

As was shown in Fig.5, the size of the mirror area increased with an increase in time-to-failure. This is the type of behaviour which would be expected if the strength of the pipe material would increase with time during annealing at 60°C .

An alternative explanation would involve the assumption that the observed effects were caused by local differences in the degree of gelation. In view of the fact that the size of the mirror area was found to vary by a factor of four (Fig.5), this explanation seems to require the assumption that rigid PVC-pipes from a given batch have a rather inhomogeneous structure. This does not seem to

be the case. In fact, the vast majority of fractures in rigid PVC-pipes seem to start at foreign particles and not within the matrix itself. The latter would have been expected if processed PVC contained a high frequency of domains with badly gelatinized resin particles.

As shown in Table 2, the thickness of the pipe wall at the point of fracture initiation was less reduced by creep for samples that showed a long time-to-failure. This indicates a change to a more brittle failure and would be the type of change expected if physical aging during testing is of importance. The increase in the size of the mirror area with lifetime suggests that crack propagation becomes the dominant fracture mechanism at longer times. This may also be interpreted as a transition to a more brittle failure. Failure caused by creep-crazing should be called brittle if the wall thickness is intact and the mirror area extends over the complete wall. This definition is in accordance with the observation that the mirror area increases with a decrease in the stress level. (7).

For rigid PVC pipes submitted to an internal pressure a possible fracture mechanism for particle-initiated fractures is outlined in Fig.8. A mirror area is created around the particle if the requirement for the energy release rate ($G_i < G < G_{1c}$) (13) is fulfilled. This occurs at time t_1 (14). The parameter t_1 , depends on the mechanical properties, size, location and orientation of the particle, the adhesion between particle and matrix and

the stress level. The time t_1 is probably also affected by aging at temperatures above $40-50^{\circ}\text{C}$. The mirror area reaches a critical size at t_2 . The major factors affecting the time (t_2-t_1) would be the stress level, the size of the pipe wall, the temperature (15) and the annealing time. The time-to-failure (t_3) might be approximated with t_2 as the crack speed increases rapidly at time t_2 . It is likely that (t_3-t_2) is fairly small as compared to t_2 (14).

ACKNOWLEDGEMENTS

The authors wish to thank Uponor AB for supplying the pipe material and KemaNord AB for carrying out the internal pressure experiments. Thanks are also due to Lars-Eric Carlsson, M.Sc. Nuclear Physics, The Lund Institute of Technology, for the PIXE-analysis and to Prof. Bertram Broberg, Department of Solid Mechanics, The Lund Institute of Technology, for valuable discussions.

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Table 1. Formulation

Pevikon S 688	100
ADWAWAX 165 (Cincinnati Milacron)	1
ADWASTAB TM-692 (Cincinnati Milacron)	0.3
Stearic acid	0.3

Table 2. The distribution in time-to-failure for the tested pipes and the final wall thickness at the point of fracture.

Sample	Time-to-failure (h)	Number of grow- ing cracks	Wall thickness at the point of fracture ¹⁾ (mm)
1	342	-	4.37
2	721	1	4.52
3	814	4	4.65
4	835	-	4.88
5	931	7	4.57
6	1019	1	4.74
7	1136	-	4.81
8	1316	1	4.96
9	1805	-	4.59

1) The nominal wall thickness of the pipe was 5.3 mm.

Table 3. PIXE-analyses of the particle shown in Fig.2.

Element	Conc. (%)	Detection limit (ppm)
S	2.86 ± 0.28	253
Cl	0.31 ± 0.03	168
K	0.016 ± 0.009	99.3
Ca	1.47 ± 0.11	92.7
Ti	3.21 ± 0.23	81.5
Mn	0.033 ± 0.004	11.0
Fe	0.032 ± 0.003	31.2
Cu	0.005 ± 0.002	50.1
Zn	2.13 ± 0.16	12.3
Total	10.066	
Rem.: H, C, N, O		

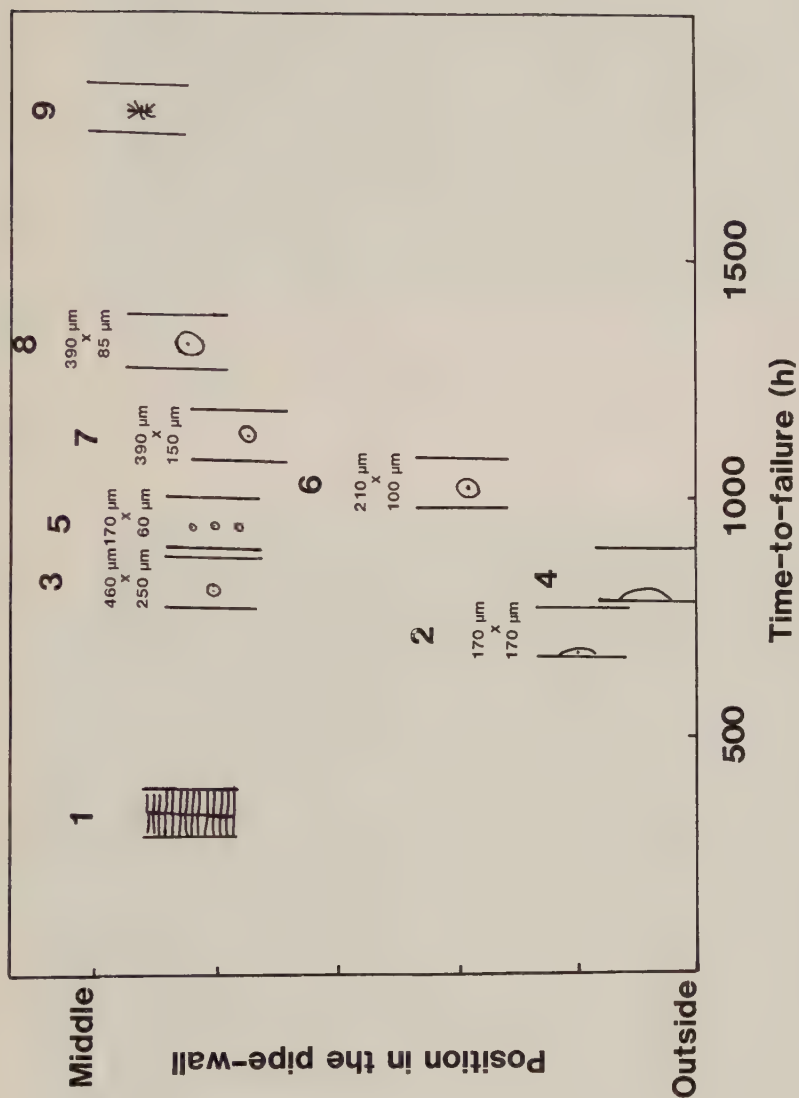


Figure 1. The scattering in time-to-failure and the nature of the fracture surfaces including the particle size and the position of the points of fracture initiation in the pipe wall.

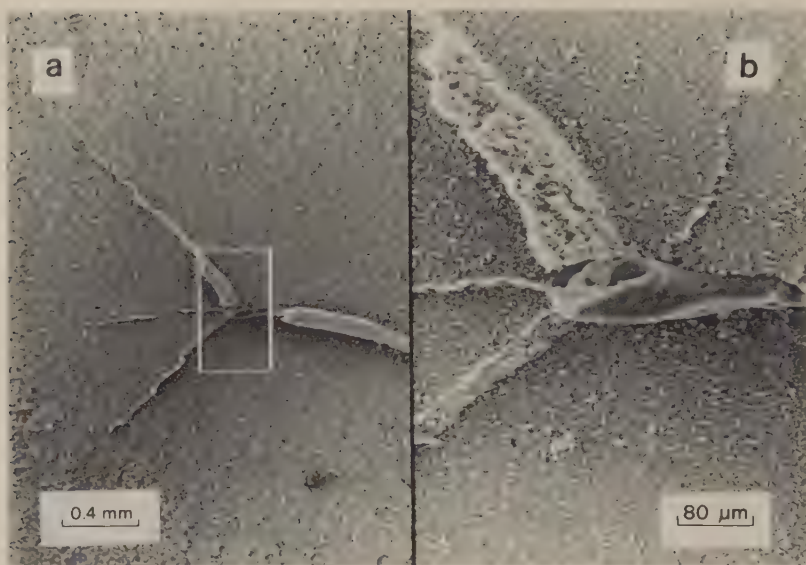


Figure 2. An example of a fracture surface containing a particle. Ripples are spreading radially from the particle (a). Enlargement of the framed area showing the particle (b).

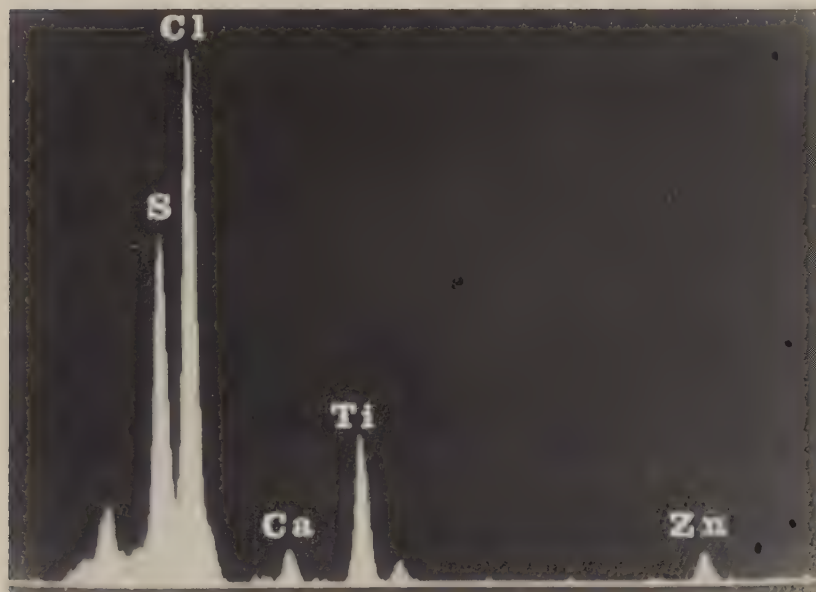


Figure 3. Energy-dispersive X-ray spectrum of the particle shown in Fig. 2.

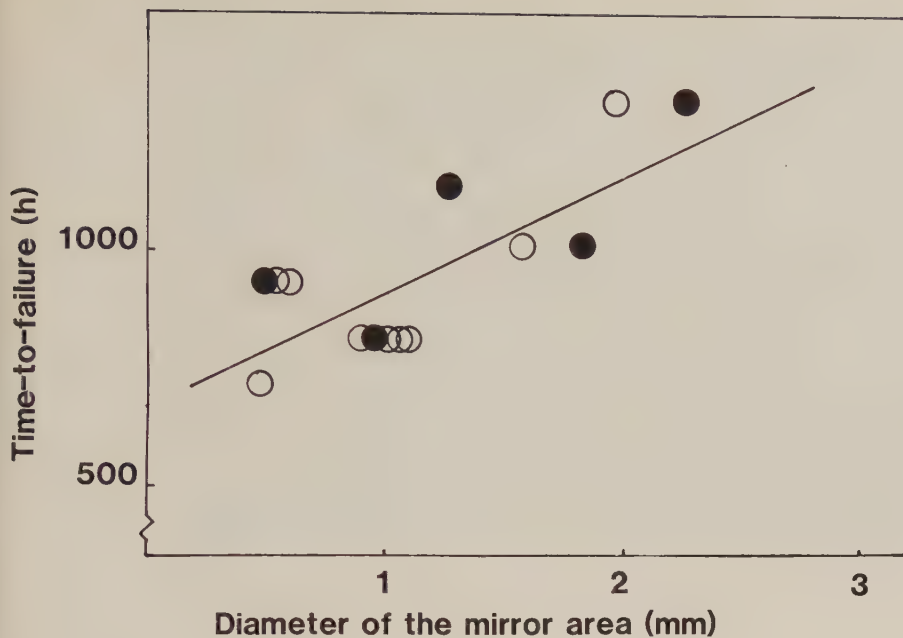


Figure 4. Effect of the time-to-failure on the size of the mirror area.

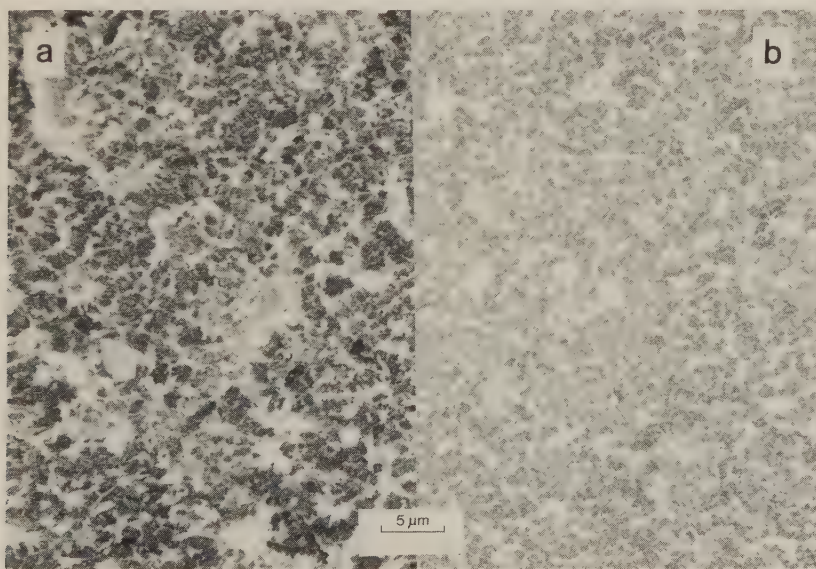


Figure 5. The structure of the mirror area changes from a rough (a) to a smooth (b) texture with increasing time-to-failure. a = 814, b = 1316 h.

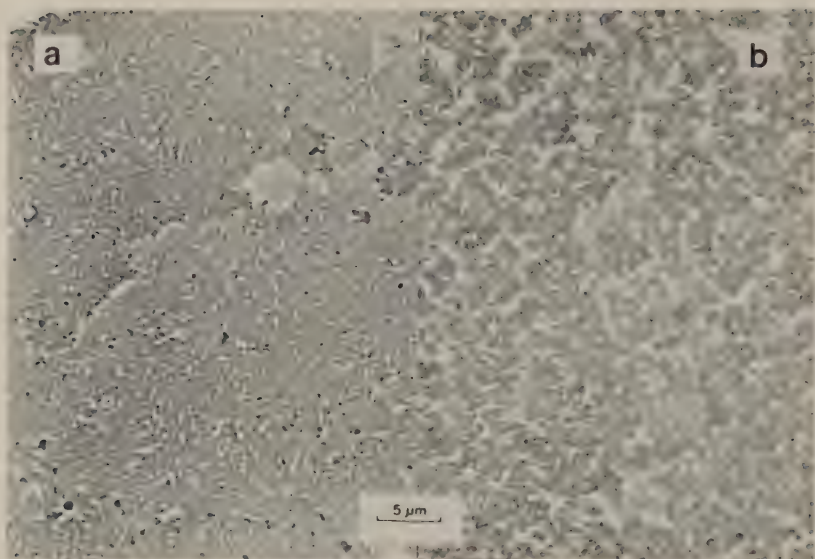


Figure 6. The structure of the mirror area is finer in a growing crack (a) than in the crack leading to failure (b).



Figure 7. The fracture surface obtained at the longest time-to-failure contained no particles but a large line defect.

Factors affecting

t_1 :

- Stress level
- Mechanical properties
- Size, location and orientation of the particle
- Adhesion particle/matrix

Factors affecting

$t_2 - t_1$:

- Stress level
- The size of the pipe-wall
- Temperature
- Annealing time

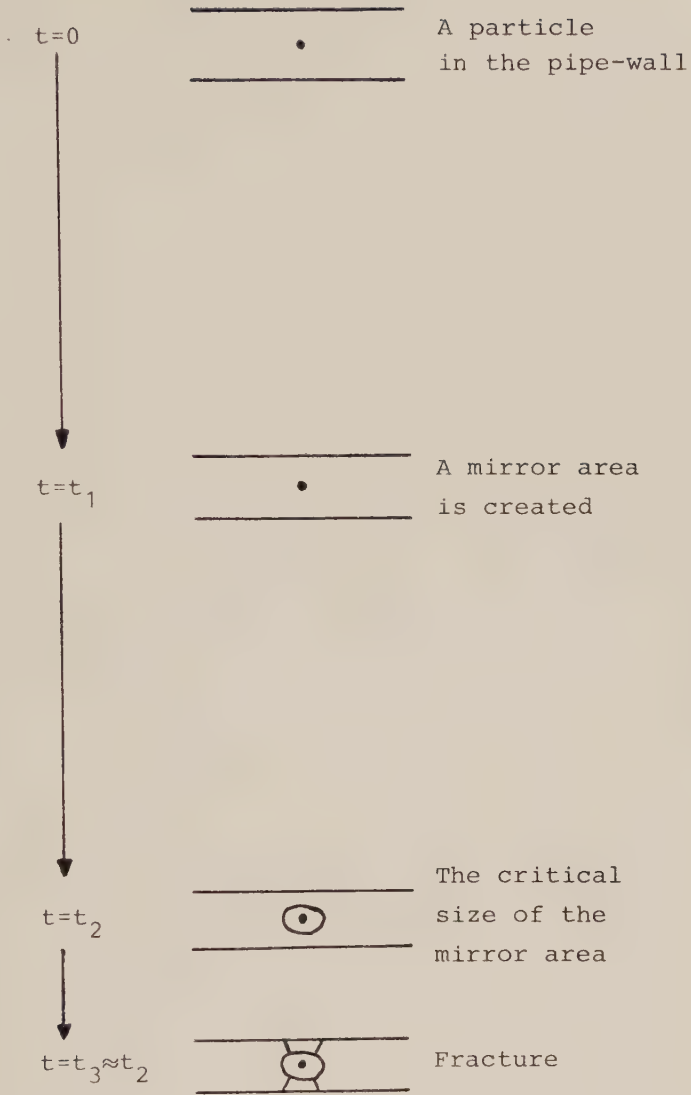


Figure 8. A possible fracture mechanism for particle-initiated fractures for rigid PVC pipes.

IV

Information about incomplete gelation in rigid PVC
from SEM studies of fracture surfaces

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Information about incomplete gelation in rigid PVC from SEM studies of fracture surfaces.

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ABSTRACT

Structural details which can be related to the presence of unmelted or incompletely gelatinized PVC resin particles can normally not be found in fracture surfaces obtained by pressure testing of PVC pipes. In a recent experimental series, however, almost entirely intact grains and seemingly undamaged primary particles were found in the fracture surface if the test was carried out at an unusually high stress level (42.5 MPa). The results indicate that there may exist certain test conditions which tend to give fracture surfaces that contain information about the degree of gelatinization.

Rigid PVC pipes are normally subjected to internal pressure tests in order to elucidate their long-term behaviour (1). The time-to-failure is a function of the stress level, the temperature and the quality of the pipes. From studies using scanning electron microscopy (SEM), it is well-known that fracture surfaces obtained in such tests may show quite different appearances (2,3). At very high stress levels, where ductile failures predominate, the fracture surfaces may be completely covered with drawn-out, rather thick polymer filaments, whereas at low stress levels, the fractures usually are more brittle. In these latter cases, the fracture surface normally contains a so-called mirror area indicating that the failure has been preceded by a period of sub-critical crack growth. Rather commonly, the mirror area grows out from a foreign particle (a filler or pigment particle or a solid impurity), which has been responsible for initiating the fracture process (2,3).

Previously, in fracture surfaces of the types discussed, we have never been able, using SEM, to observe structural details which can be related to the structure of the original PVC resin particles. Indications that such structures may be present in PVC pipes had been obtained, however, by transmission electron microscopy using thin sections of embedded samples (4). We can now report that by using the SEM technique, we have been able to observe in several fracture surfaces almost entirely intact suspension resin particles as well as seemingly undamaged primary particles. Examples of this are shown in Figs. 1-4.

The observations were made in fracture surfaces formed after fracture initiation along a line running down the middle of the pipe-wall as shown in Fig. 1. The fracture surfaces, when seen from the side, were V-shaped, i.e. a cavity had been formed in the pipe-wall before the final fracture occurred. This is due to the ductile failure with tearing of the matrix during fracture propagation. The micrograph reproduced in Fig. 2 shows the presence of two suspension resin particles at the line of initiation. However, the main part of the line defect consisted of PVC-filaments of 0.1-1 μ m in diameter (Fig.3). At a higher magnification, primary particles could also be seen in some parts of the surface. The last example (Fig.4) shows a glass fibre between the PVC-matrix and a resin particle at the line of fracture initiation. Even in this case, primary particles were observed in some parts of the fracture surface at a higher magnification.

The result reported here were obtained in a recent experimental series in which PVC pipes were tested at a rather broad range of stress levels. The fracture surfaces which contained structures pointing to an incomplete gelation were obtained at rather high stress levels (42.5 MPa at 20°C and 18 MPa at 60°C) and hence relatively short fracture times (4-35 h).

The pipes samples were produced on a twin-screw extruder (Krauss-Maffei KMD 90) using four formulations differing with respect to the filler only (no filler, chalk, glass balls and glass fibres). When tested at the stress levels

given above, incompletely gelatinized PVC was observed in pipes from all of the four formulations.

The results indicate that it may be possible to detect incomplete gelation in rigid PVC by SEM studies of fracture surfaces if these are formed in experiments carried out at a suitable stress level or at a certain strain rate.

A method which would be able to detect local areas containing more or less unmelted material in processed PVC would be very helpful in studies of PVC processing. Experiments designed to learn more about the possibility of using SEM to obtain such information are under way.

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Figure 1. Fracture initiation along a line running down the middle of a rigid PVC pipe.



Figure 2. Two S-PVC resin particles at the line of fracture initiation.

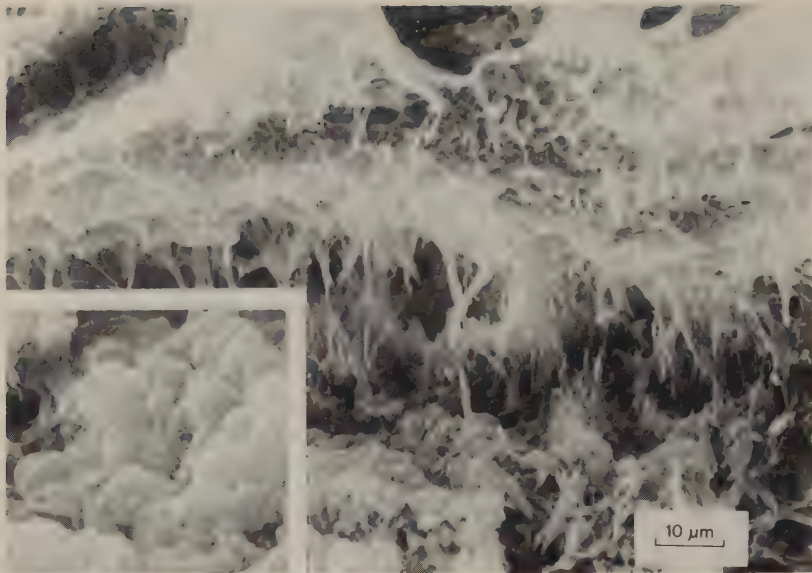


Figure 3. The main part of the line defect consisted of PVC-filaments of 0.1-1 μm in diameter. At a higher magnification, primary particles could also be seen in some parts of the fracture surface (inset).

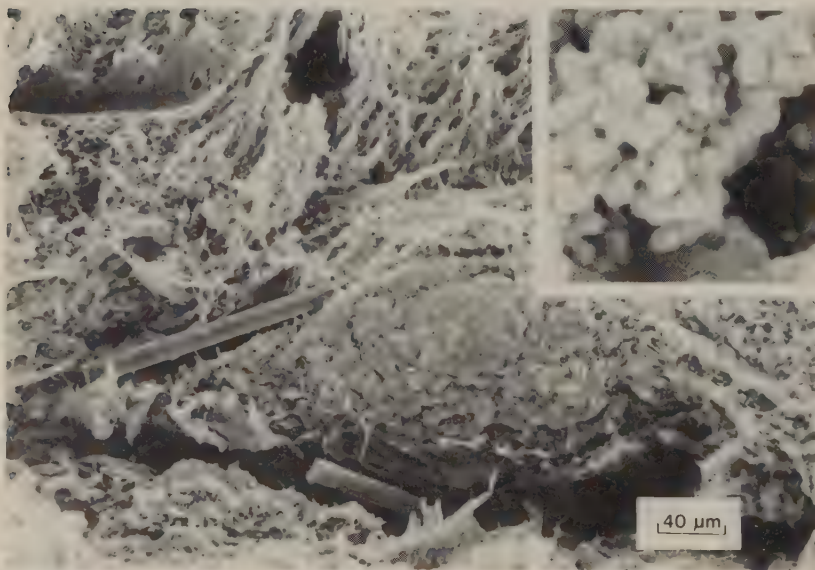


Figure 4. A glass fibre between the PVC-matrix and a resin particle at the line of fracture initiation. At a higher magnification, primary particles were observed in some parts of the fracture surface (inset).

V

Tensile creep-tests, internal pressure tests and scanning electron microscopy of electrical conduits of PVC.

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Tensile creep-tests, internal pressure tests and scanning electron microscopy of electrical conduits of PVC.

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ABSTRACT

Electrical conduits prepared from a mixture of suspension and emulsion PVC resin were subjected to an internal pressure test. The ability to withstand internal pressure was found to be slightly reduced by an increase in the amount of lubricant. Tensile tests at constant load resulted in a lower initial creep rate for an increased amount of lubricant. The pipe samples from the two test methods were investigated by scanning electron microscopy. A skin-like structure was found in the fracture surfaces formed at an intermediate stress level in the internal pressure test. This structure was not observed in the fracture surfaces obtained in the notched tensile tests at constant load.

In a previous investigation, scanning electron microscopy (SEM) was used to study fracture surfaces in PVC pipes tested at relatively high internal pressures. It was frequently observed that the fracture surfaces contained seemingly undamaged primary particles and in some cases, almost entirely intact resin grains (1). These observations suggested that fracture surfaces obtained at certain high stress levels might provide information about the internal structure of the processed polymer. This idea was followed up in the present investigation.

The present study was carried out using, as test samples, electrical conduits prepared from a mixture of suspension and emulsion PVC resins. This type of pipe was chosen because a previous study in this laboratory (2) had indicated that the emulsion PVC particles did not melt completely during processing of such a formulation. It could be expected, therefore, that this type of test sample contained some inhomogeneities which might show up in fracture surfaces formed at certain high stress levels.

In this study, two sets of samples, differing in the extent of gelation were used. The fracture surfaces studied were obtained in two different types of tests; internal pressure tests at constant pressure and notched tensile tests at constant load. Both types of experiments covered a range of fracture times extending from minutes to several weeks.

MATERIALS AND METHODS

Samples

The samples were electrical conduits having a nominal external diameter of 22 mm and a wall thickness of 2.0 mm. One set of samples was taken from the normal production line of Uponor AB, Sweden. The other set was prepared in an experimental run, using a formulation which differed from that used in the production line only by its higher content of lubricant (0.35 instead of 0.25 phr). This would give samples with a somewhat lower level of gelation.

Tensile tests

The pipes were subjected to a constant load test at 60°C, using the equipment shown in Fig. 1. The total load was varied within a range of 140 to 200 kg, corresponding to nominal stresses of 1.2 to 1.7 MPa. Only 40 % of the pipe length was kept at 60°C in order to avoid an early failure at the end fittings. All fracture surfaces studied were obtained in tests using notched samples. Separate experiments using unnotched samples were carried out in order to determine tensile creep rate.

Internal pressure tests

The internal pressure tests were also run at 60°C. The tests were carried out at nominal stresses of 9.5 to 20 MPa. In the normal testing procedure, the samples were annealed for

1 h at 60°C before application of the pressure. The effect of annealing time on fracture time and fracture surface appearance was studied in a few tests at 9.5 MPa.

Fractography

The fracture surfaces were investigated in a scanning electron microscope (ISI 100 A). The samples were sputter coated with gold/palladium prior to the fractographic investigation.

RESULTS

Experiments at constant internal pressure

Fracture times at different stress levels for the two sets of samples are shown in Fig. 2. It seems that increasing the amount of lubricant from 0.25 to 0.35 phr was followed by a slight decrease in fracture time at the lower stress levels studied. This is in agreement with the expected effect of decreasing the level of gelation by increasing the amount of lubrication. Fig 2 also shows that prolonged annealing at 60°C increased the fracture time.

The fractographic studies showed that the structure of the fracture surfaces varied considerably with the stress level or with fracture time. However, none of the fracture surfaces studied showed structural details that could be explained as being due to unmelted emulsion particles, unbroken primary particles or larger fragments of the suspension resin grains. With reference to the previous observations

referred to in the introduction, this was a rather unexpected result.

The fracture surfaces obtained at the highest stress levels (Fig. 3), had the typical appearance of a uniform ductile fracture. It seems that the elastic energy under these conditions was sufficiently large to permit the fracture to propagate in any direction. At intermediate stress levels, the fracture surfaces became more complex and there appeared within the fracture surface areas having an unusual structure which can best be described as skin-like. This is illustrated in Fig. 4. The surface of the skin was much smoother than that of so-called mirror areas often found in fracture surfaces of PVC pipes. The relative amount of the skin-like structured areas in the fracture surfaces varied with the stress level in both sets of pipes. In each set, however, the largest relative amount of skin-like structure was found in samples subjected to a nominal stress of 13 MPa. Fig. 5 shows the relative amount of skin-like structure in the fracture surfaces as a function of fracture time. It can be seen that this type of structure was found primarily at rather short fracture times.

For the sample with the higher amount of lubricant skin-like structures appeared over a wider range in fracture time and with more scatter. This indicates that the occurrence of skin-like areas in the fracture surfaces is related in some way to the internal structure of the processed polymer.

At the lower end of the stress range the fracture surfaces showed the typical mirror area structure (Fig. 6) formed in most fractures at long fracture times (3,4). Annealing, which according to Fig. 2 produced an increase in fracture time was followed by an increase in the size of the mirror area. This indicates that annealing stiffens the material and tends to favour a more brittle failure, a behaviour which is in line with the results in Fig. 7, which shows that annealing leads to a decrease in the creep rate (see Fig. 7).

The origin of the peculiar skin-like structure observed in this study is not quite obvious. We have never encountered such structures in fracture studies of normal PVC pressure pipes prepared from all-suspension PVC. It is likely that these structures were formed in a process in which creep flow was much less extensive than in the process giving the surrounding areas their much coarser structure. This is equivalent to saying that the skin-like areas were formed in a more brittle failure than the rest of the surface. If the complex fracture surface appearance shown in Fig. 4 indicates structural inhomogeneities in the processed PVC, the skin-like areas would correspond to domains with a better than average degree of gelation. This suggestion is based upon the observation that, above a certain level of gelation, further improvement in gelation is often followed by a decrease in the impact strength (5).

Tensile fracture and tensile creep

The pipes prepared from the formulation with the higher amount of lubricant showed a lower initial creep-rate than the others. This is seen from the creep curves in Fig. 7. Each of these curves is based on results from triplicate runs. It was not expected that a decrease in the level of gelation should give such an effect. A possible explanation would be that the lower creep-rate observed with the less well gelatinized pipes was due to a less pronounced axial orientation of the material. The fact that the two sets of pipes were prepared on different occasions may have contributed to this effect.

Annealing, which led to a drastic decrease in the creep-rate (Fig. 7), also gave a longer life-time in the notched tensile test and a lower ultimate elongation. In these respects, annealing had an effect similar to that obtained by decreasing the load (c f Fig. 8).

The tensile fractures started at the notches except for two of the samples, in which the failure was initiated by the formation of a so-called diamond cavity. (6). At the bottom of these cavities, structures were observed that indicated that the failure was initiated by incompletely melted resin. SEM-studies of the other fracture surfaces showed no clear, direct signs of structures which could be easily referred to the particulate nature of the original PVC resins. In some but a very few cases, and then only at isolated points, the fracture surfaces showed structures which might reflect

the internal structure of the material. The type of skin-structure discussed in the previous section was not found in any of the fracture surfaces formed in tension. This difference in fracture appearance may have several explanations. Firstly, in the internal pressure tests the pipes failed at their weakest points, whereas in the tensile test the fracture almost always occurred at the notch. Secondly, the state of orientation and the stress fields were quite different in the two types of test.

CONCLUSIONS

Incompletely melted primary particles or other fragments of resin grains were not observed in any of the fracture surfaces studied in this work. It is possible that the test samples used were more uniformly melted and gelatinized than the pressure pipes studied previously. The inhomogeneous structure of the electrical conduits, resulting from their being made of a mixture of suspension and emulsion PVC, was not reflected in the fracture surfaces. It was found, however, that fracture surfaces formed in internal pressure tests at high stress levels (around 13 MPa) contained areas with a peculiar, skin-like structure. The occurrence of this structure seemed to vary in samples differing in the level of gelation.

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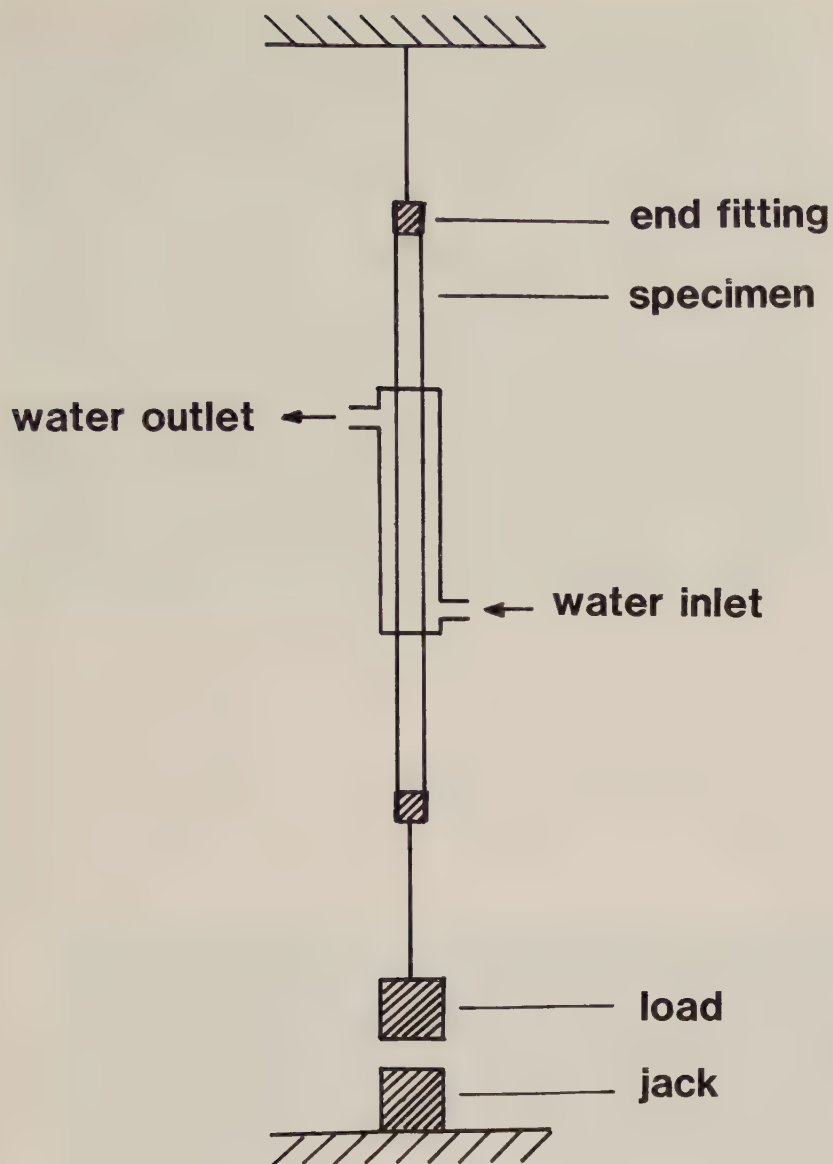


Figure 1. Testing equipment for the tensile tests at constant load.

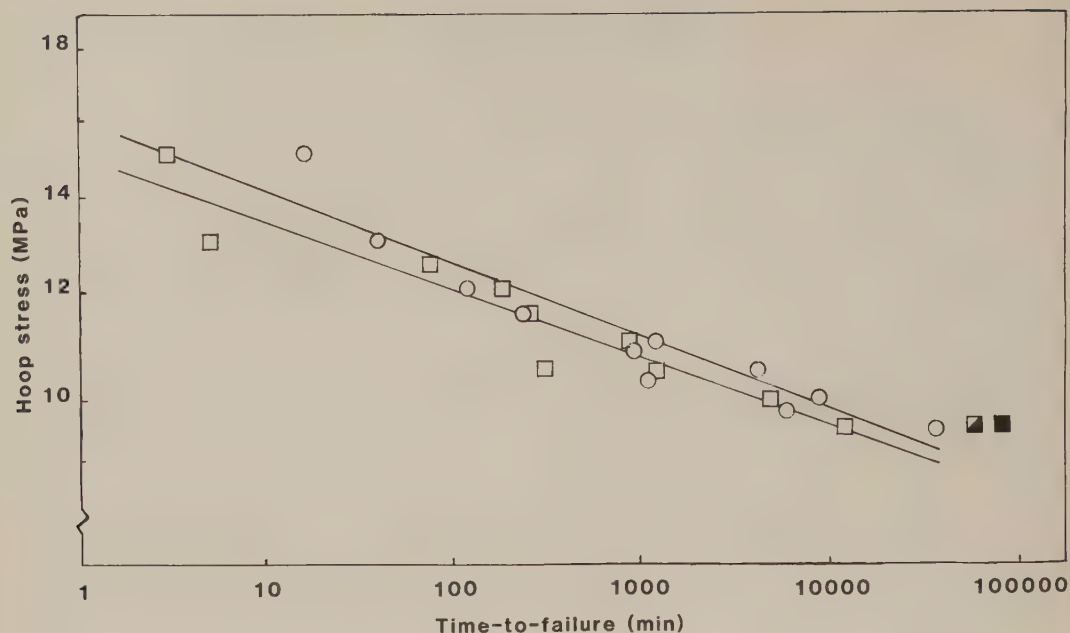


Figure 2. Effect of gelation level on resistance to an internal pressure test at 60°C. Amount of lubricant: (○) = 0.25 phr PVC; (□) = 0.35 phr PVC; Annealing time: (○)(□) = 1 h, (◼) = 200 h; (■) = 500 h.

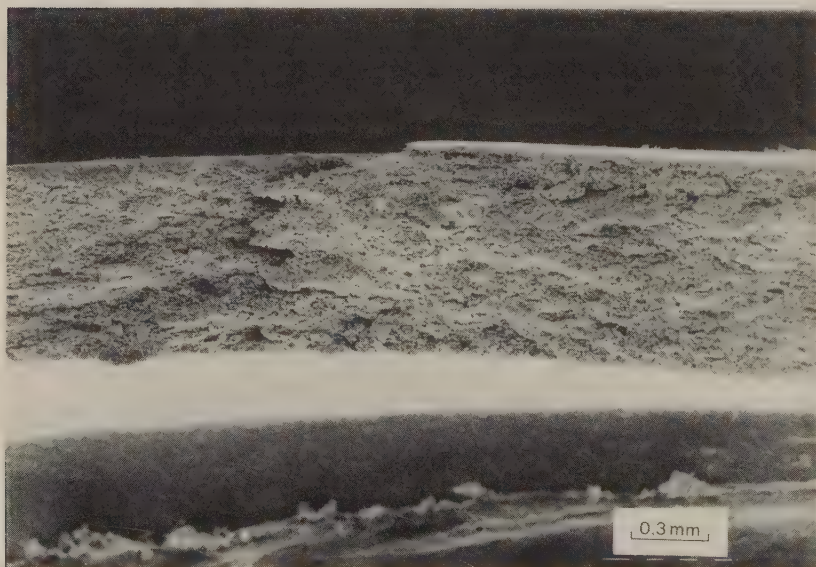


Figure 3. Fracture surface of a PVC pipe obtained at a high stress level.

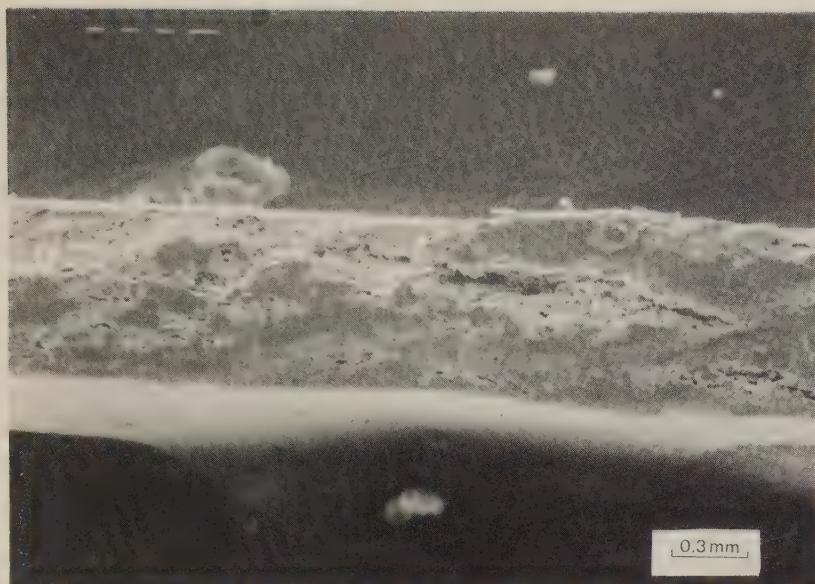


Figure 4. A skin-like structure in a PVC pipe appearing at an intermediate stress level.

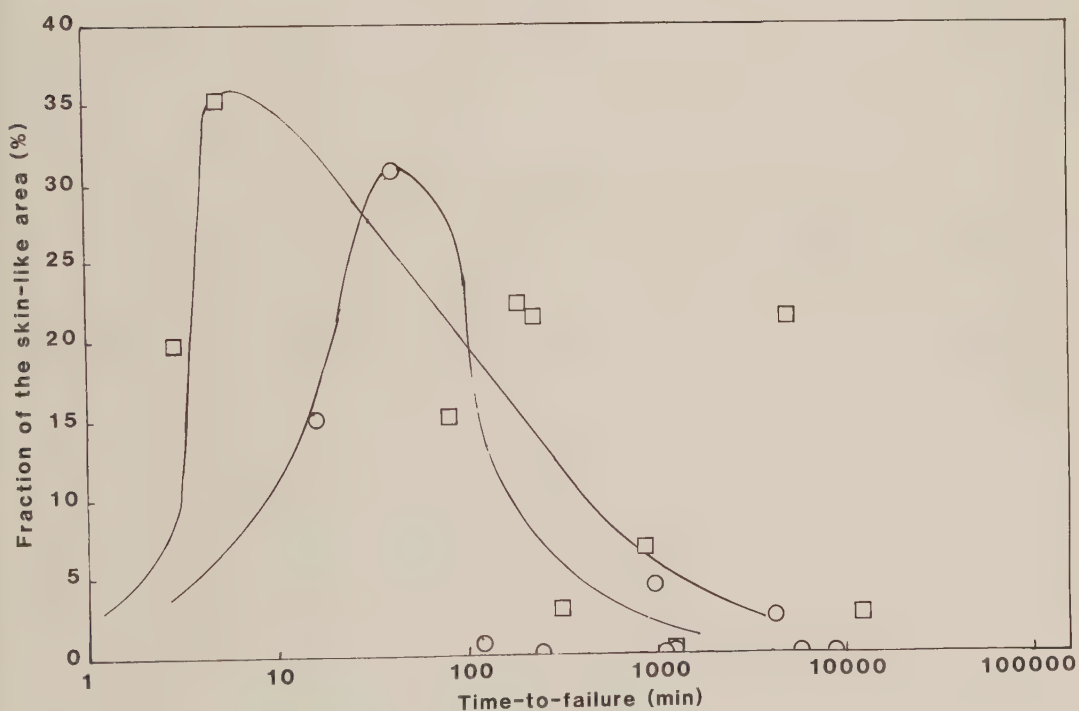
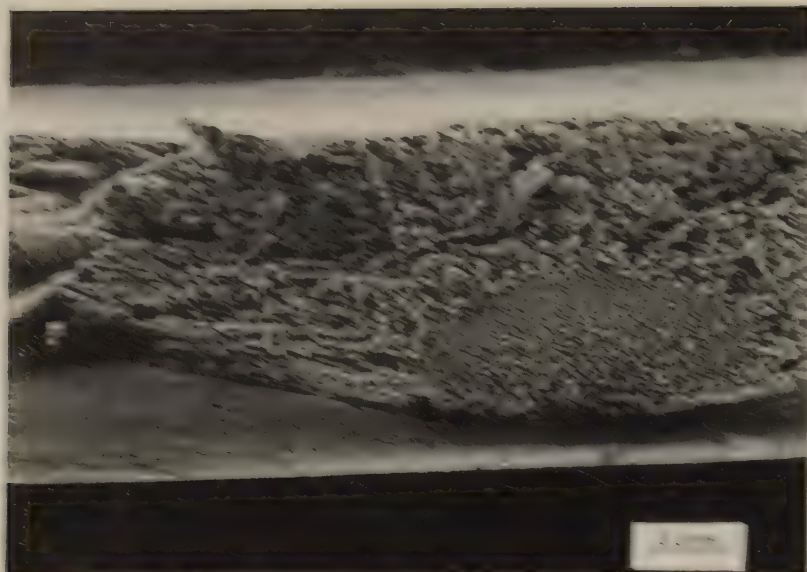


Figure 5. The relative amount of skin-like structure in the fracture surfaces as a function of time-to-failure.

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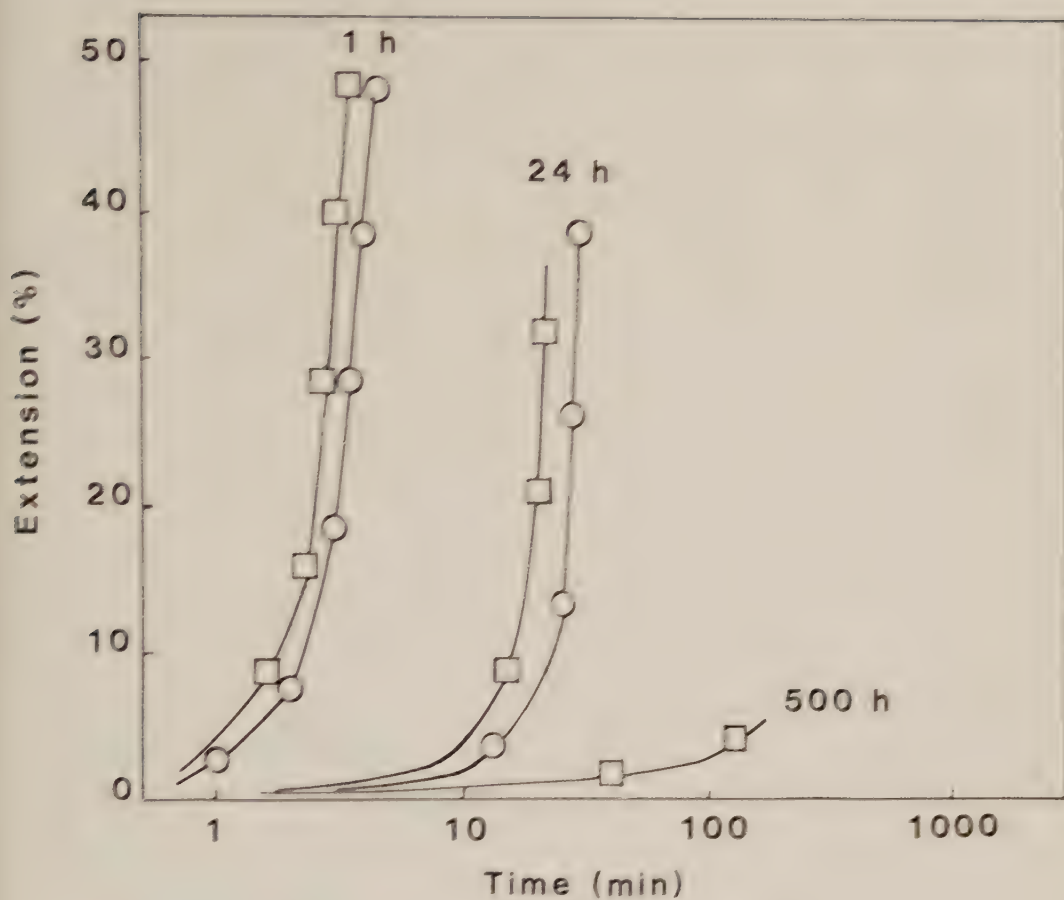


Figure 7. Creep curves obtained at a constant load of 253 kg for different annealing times.
Amount of lubricant: (□) = 0.25 phr PVC, (○) = 0.35 phr PVC.

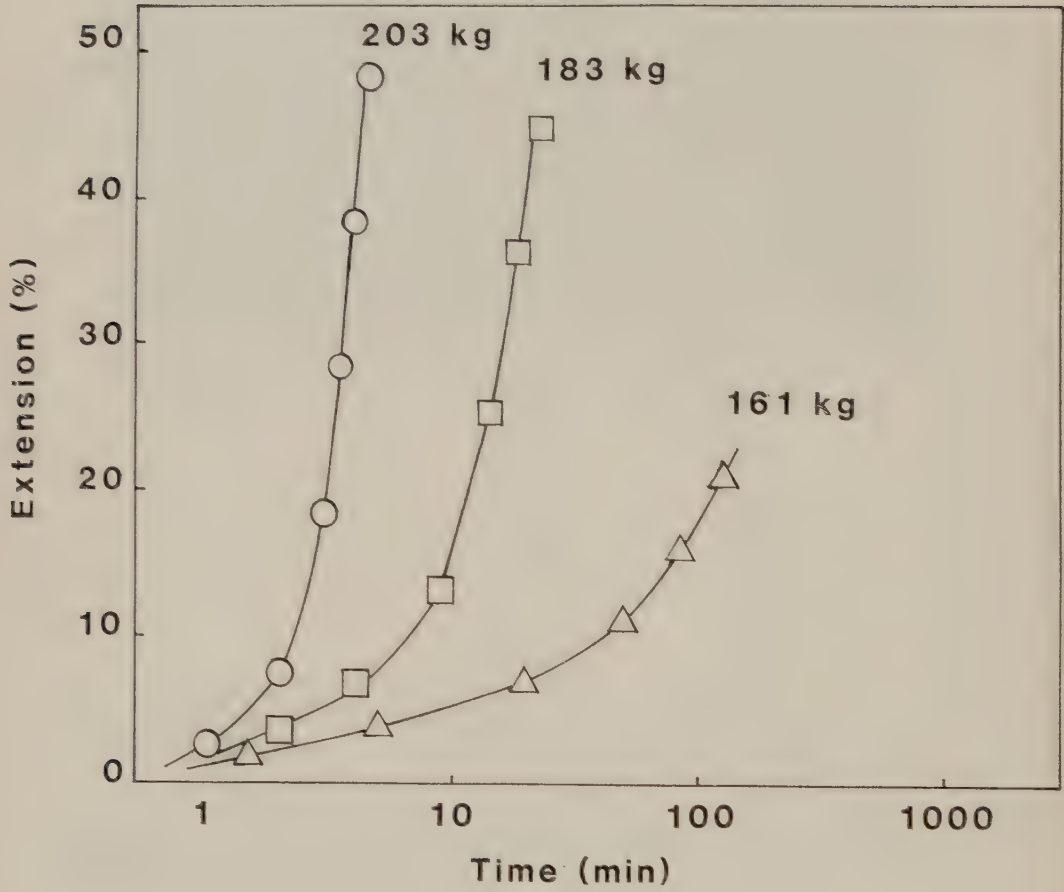


Figure 8. Creep curves obtained at a constant amount of lubricant: 0.35 phr PVC, Load: (○) = 203 kg, (□) = 183 kg, (△) = 161 kg.

VI

The distribution of lead in lead-stabilized rigid PVC pipes,
as studied by scanning electron microscopy

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ABSTRACT

Samples with flat, smooth surfaces were removed from rigid PVC pipes using a diamond saw. These were then studied in a scanning electron microscope fitted with a Robinson detector and an environmental cell, which gives an image of the back-scattered electron intensity. In such images, lead-containing particles appeared as bright spots against a dark background. This is due to the fact that the intensity of the back-scattered electrons increases with atomic number. It is shown that this method can be used to study the effect of different processing conditions on the distribution of the stabilizer in lead-stabilized rigid PVC.

INTRODUCTION

In Europe, rigid PVC pipes are normally produced using lead-stabilized formulations. The lead-stabilizers are solid substances that do not melt or dissolve in the plastic mass during processing. In the processed products, therefore, most of the stabilizer will be present in particulate form. This means that it would be of interest to study the distribution of lead in lead-stabilized PVC and to see how this distribution is affected by changes in the processing conditions.

It is possible to observe lead-containing particles using transmission electron microscopy. This technique, however, requires ultrathin sectioning and only gives information from very small areas. It would be much more convenient to use scanning electron microscopy (SEM) instead. This was done by Draguan et al. who used wave-length dispersive X-ray analysis to study the distribution of lead in a PVC sample processed in a Brabender plastograph (1). This method requires high beam fluxes and consequently results in severe beam damage. Less beam damage would be obtained by using energy dispersive X-ray analysis, but this method is not sufficiently sensitive to permit lead to be determined at the low concentrations normally used in PVC-formulations. A better alternative would be to use back-scattered electron imaging in a scanning electron microscope. The back-scattered electrons can be detected by a Robinson detector (2). The signal from this detector increases with the average specimen atomic number. The large atomic num-

ber difference between lead and chlorine would make it possible to see lead-containing domains in PVC as bright areas against a darker background. A great advantage of this method is that it allows study of very large samples.

In order not to disturb the atomic number contrast provided by the Robinson detector, the samples to be analysed should have flat, smooth surfaces. In this work, the samples were studied without a conductive coating, which was made possible by using an environmental cell modification which allowed measurements at a pressure of 0.5 torr in the sample chamber.

EXPERIMENTAL

Materials

The samples studied were rigid PVC pipes prepared from a formulation based on a suspension resin (Pevikon S684 from KemaNord) and a lead-stabilizer (Tribasic lead sulfate, 1.5 phr and Dibasic lead sulfate, 0.5 phr). Two sets of samples were used. In one set (samples 1-4) the level of gelation was varied by using different amounts of lubricant (Paraffin wax, 0.26-0.62 phr); in the other (samples 5-11) the level of gelation was varied by processing at different mass temperatures ranging from 176 to 205°C. Samples 1-4 had been subjected to internal pressure tests at 60°C before being used in this study. The other samples were used as produced.

The pipes were cut radially by a diamond saw so that flat,

smooth surfaces were obtained. One of the cut surfaces was studied in the SEM and the other was used for determining the level of gelation using a standard methylene chloride test (Wavinorm 14.001). For some of the samples, the lead distribution was also studied after annealing at 100°C for 14 days.

Scanning electron microscopy

The samples were studied in a scanning electron microscope (ISI 100 A) fitted with a Robinson detector. The microscope was also fitted with an environmental cell (3). This consists of a modification of the vacuum system and enables pressures of between 0.1 torr and 1 torr to be maintained in the specimen chamber, while the beam is generated in the high vacuum electron optics column. The gas molecules in the sample chamber dissipate the electric charge on the sample and the specimen can be examined without the need for conductive coating. The microscope operated at a relative high accelerating voltage (35keV) in order to suppress the topographic contrast. A magnification of 2000X was chosen in order to get optimum performance with respect to resolution and beam damage.

RESULTS AND DISCUSSION

Figs. 1a and 1b show the same sample area as observed using the normal secondary electron detector and a Robinson detector, respectively. As the sample had a flat, smooth surface, the image obtained from the secondary electron detector, which gives good topographic contrast but poor atomic

number contrast, contained very little information. The Robinson detector, however, which can be characterized as having a good atomic number contrast, gave an image which showed a large number of bright spots which were identified as lead-containing domains. This identification was confirmed by X-ray energy dispersive analysis of the sample at points corresponding to bright domains having a size larger than $2\text{ }\mu\text{m}$. In images obtained from the Robinson detector, it was often possible to distinguish, besides distinct bright spots, areas which may be described as "clouds" of lead.

Fig. 2 gives the lead domain size distribution as calculated for samples 5-11 from micrographs that in each case covered an area of $115 \cdot 10^{-6}\text{ cm}^2$. The lower size limit of bright spots calculated as lead-containing particles was $0.25\text{ }\mu\text{m}$. A study of the same samples using the PIXE-technique showed that the samples had the same average lead content. It is evident from Fig. 2 that the lead particle size distribution was affected by the processing conditions. As the mass temperature was increased from 176 to 190°C , the particles became less distinct (Fig. 3) This was accompanied by a decrease in the number of small particles detected, possibly due to the fact that small diffuse particles may not be resolved. The interface particle/matrix became more distinct above 190°C and this was accompanied by a gradual increase in the number of small particles up to 205°C .

Fig. 2 indicates that almost the same particle size distribution was obtained at the lowest and the highest processing

temperature. However, the actual images showed that there were certain areas in the sample processed at the lowest temperature (Fig. 4) which were almost free from lead particles, whereas the stabilizer was much more evenly distributed in the sample processed at the highest temperature.

As samples 1-4 had been subjected to internal tests at 60°C, the size of the lead domains might have been affected by the test. The effect of annealing at 100°C was studied for the sample processed at 176°C. The result indicated that annealing at 100°C for 14 days had no influence on the size distribution of the lead domains. This might indicate that the internal pressure test at 60°C had no effect on the lead distribution.

The lead-domain size distribution for samples containing different amounts of lubricant is shown in Fig.5 . In this case, the sample with the lowest amount of lubricant had the highest level of gelation as determined from methylene chloride tests, tests of resistance towards internal pressure as well as of impact strength (4). This sample had a particle size distribution which was quite similar to that of the 190°C sample in Fig. 2 , which in that series was the sample that had the greatest impact strength (5). It is possible that further work may show that there is a correlation between the lead-domain size distribution and its uniformity over larger areas on the one hand and the extent of gelation on the other.

Fig. 5 gives results for two samples (2 and 3) containing the same amount of lubricant but processed at different times. Sample 2 showed good long-term behaviour in the internal pressure test and good resistance to methylene chloride. Its lead domain size distribution was similar to that of the good sample 1. Sample 3, however, failed very early in the internal pressure test. The present study of the distribution of the stabilizer indicated, however, that this was due to an inhomogeneous gelation of the sample. This was inferred from the fact that the back-scattered electron image showed that this sample contained areas with predominantly large and other areas with predominantly small lead-containing domains.

CONCLUSIONS

Back-scattered electron imaging in a scanning electron microscope makes it possible to study the effect of different processing conditions on the distribution of lead in lead-stabilized rigid PVC.

This new method is qualitative and relative, yet the advantages are obvious; a quick method for studying large sample surfaces without the need for any sample preparation.

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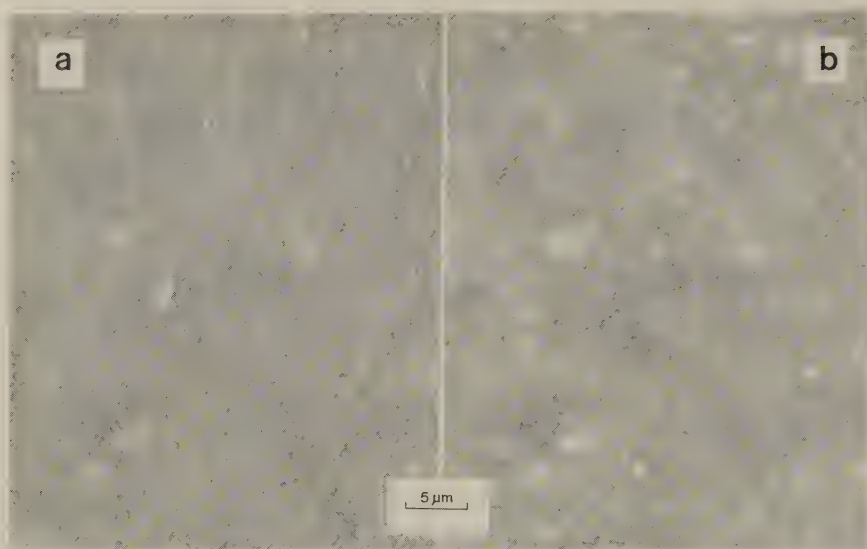


Figure 1. A poor atomic number contrast is obtained by a secondary electron detector (a). Lead-containing domains show up in the same area when using a Robinson detector (b).

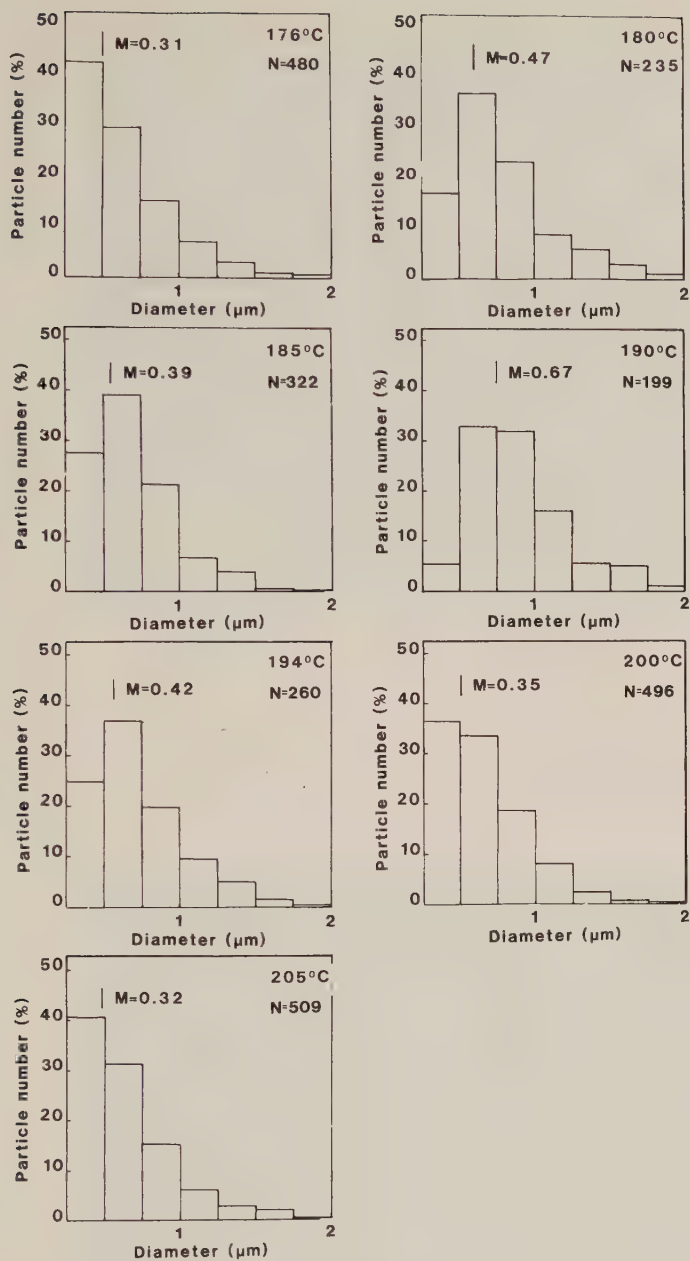


Figure 2. Lead domain size distribution for different mass-temperatures.



Figure 3. The lead-domain particles appear less distinct at a mass temperature of 190°C .

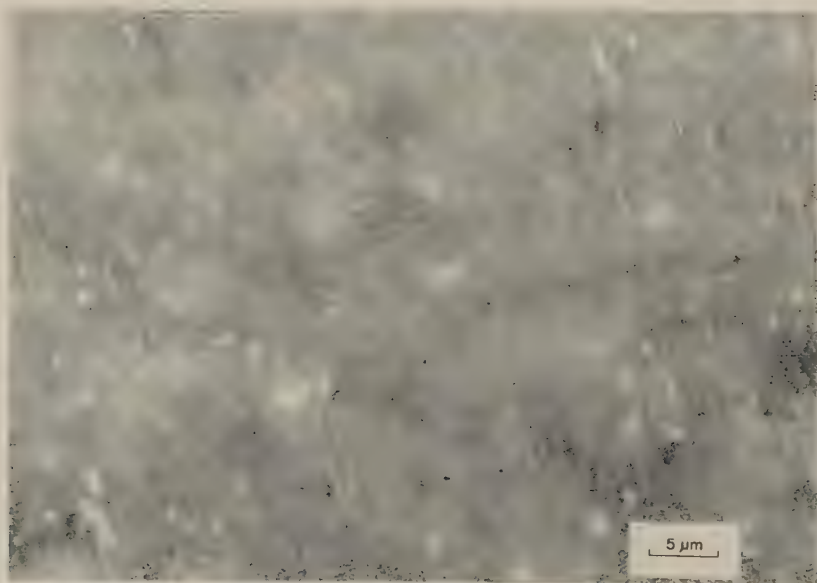


Figure 4. An uneven distribution of the lead domain particles is obtained at the lowest processing temperature (176°C)

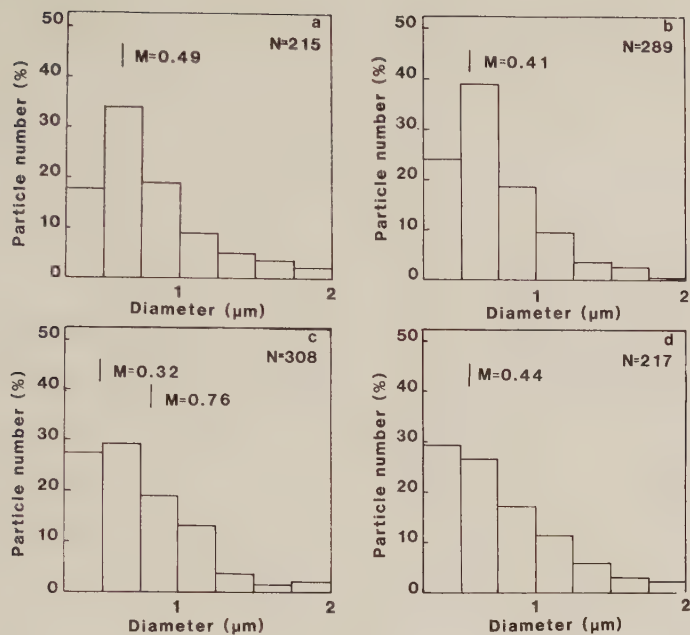


Figure 5. Lead domain size distribution for different amounts of lubricant: (a) = 0.26 phr PVC; (b) (c) = 0.36 phr PVC; (d) = 0.62 phr PVC.

VII

A combination of electron irradiation and the methylene chloride test for obtaining the level of gelation.

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ABSTRACT

A method is described which permits a determination of the level of gelation in well gelatinized rigid PVC. The method consists of estimating the lowest dose of electron irradiation that is required to produce an increased attack by methylene chloride. A low dose corresponds to a high level of gelation. The test requires the use of samples with flat, smooth surfaces.

INTRODUCTION

The quality of rigid PVC products is highly dependent on the level of gelation, a property that may be estimated in a number of different ways. Among existing methods, the best results are probably obtained by capillary rheometry measurements (1,2). However, since this method requires the use of fairly large samples, it cannot give information on local variations in the gelation level. Another type of test, which can provide this information, is based on analysing the surface defects produced by subjecting the sample to methylene chloride under standardized conditions (3). A great weakness of this type of method is that it cannot differentiate between samples which have reached high levels of gelation. The reason for this is that methylene chloride does not produce a significant surface attack at levels of gelation above a certain, fairly moderate level.

However, results to be presented in this paper indicate that it is possible to extend the useful range of the methylene chloride test by comparing the surface attack caused by the combined action of electron irradiation and of methylene chloride. The electron irradiation, which can be carried out in a scanning electron microscope, causes a certain amount of beam damage which makes the sample more susceptible to attack by methylene chloride. Samples with a high level of gelation are very resistant to methylene chloride and for such samples an increased attack can be observed even after very low doses of irradiation. The

proposed method consists in finding the lowest dose that produces an increased attack after treatment with methylene chloride. Thus, a low dose corresponds to a high level of gelation and a high dose indicates that the sample is less well gelatinized.

PROPOSED METHOD

A sample of processed, rigid PVC, having a flat, smooth surface is prepared using a diamond saw. The sample is then inserted into a scanning electron microscope and a succession of several small areas (about $45 \times 65 \mu\text{m}$) are irradiated during equal times using successively higher beam currents. The sample is then submerged in methylene chloride at 19°C for 20 minutes, and is afterwards inspected using an optical microscope.

By observing the number of irradiated areas that have suffered a stronger attack by methylene chloride than the unirradiated surroundings, it is possible to find the lowest dose of irradiation that caused an increased attack. This dose is an inverse measure of the level of gelation; i.e. the lower the dose, the higher is the level of gelation.

EXPERIMENTAL

Sample preparation

As the method is based on comparing the surface roughness of irradiated areas on unirradiated surfaces after treat-

ment with methylene chloride, it is essential that the original surface is as smooth as possible. In this work, therefore, pipe samples with flat, smooth surfaces were cut by a diamond saw. (Isocut, Mikron AB, Sweden).

Electron irradiation

The samples were irradiated in a scanning electron microscope (ISI 100A) fitted with an environmental cell (4). By using a plug in the line between the oil diffusion pump and the sample chamber, it is possible to work with air or nitrogen in the sample chamber at pressures up to 1 torr with this system (cf. Fig. 1). During operation, the gas molecules dissipate the charge built up on the sample surface so that nonconducting samples like PVC can be studied without a conductive coating.

A Robinson back-scattered electron detector (5) was used for focusing the electron beam. The irradiation conditions used are given in Table 1. At each beam current setting, an area of about $45 \times 65 \mu\text{m}$ was irradiated. In general, seven areas were irradiated on each sample. Before each irradiation experiment, the beam current was measured using an electrometer (Keitley Instrument 610 C) connected to the sample holder. The measurements consisted of moving the electron beam spot to the centre of a small hole ($\varnothing 0.6 \text{ mm}$) drilled in the sample holder close to the sample and taking the electrometer reading as a measure of the beam current.

RESULTS AND DISCUSSION

In a light microscope, it is possible to observe a faint yellow coloration of an uncoated PVC surface that has been subjected to an intense irradiation in a scanning electron microscope. The color is due to the formation of conjugated double bonds and is a consequence of dehydrochlorination induced by irradiation. This type of beam damage occurred only at exposures above $7 \cdot 10^{-4} \text{ Q/cm}^2$. At lower doses, no beam damage could be observed in the light microscope. In these cases, however, treatment of the sample with methylene chloride often made the irradiated areas visible. They then appeared as having a more pronounced surface roughness than the non-irradiated surrounding areas. The dose that made it possible to differentiate between an irradiated area and its non-irradiated surrounding was found to vary with the level of gelation of the PVC sample. This is illustrated by the data in Fig. 2. This figure summarizes results obtained with three pipe samples differing in the level of gelation. The drawings illustrate the appearance of the samples after being subjected to a standardized methylene chloride test (Wavinorm 14.001). The left column gives the corresponding data for the level of gelation. For the upper sample the level of gelation was above the range covered by the methylene chloride test. The right column gives the lowest irradiation dose necessary to give an increased attack in the methylene chloride test. For two of the samples, two dose values are given. These refer to results obtained from studies at different positions on the samples, as indicated on the schematic

drawings. As can be seen, the dose values corresponding to the "unattacked" positions of the three samples differed considerably. The reason for this is that there was a certain surface roughness in the "unattacked" positions as well, a roughness that increased in going from the upper to the lower sample. The higher dose for the lower sample simply means that in this case a more extensive beam damage was required in order to increase the surface roughness to an extent which was observable in the light microscope. The electron irradiation thus can be thought of as a means of quantifying the surface roughness.

By using the proposed method it thus seems possible to arrive at a value, the minimum exposure which gives an increased methylene chloride attack; this value can serve as a quantitative measure of the level of gelation. This works well except at very low levels of gelation, where the methylene chloride strongly attacks a non-irradiated surface. Such a case is illustrated by the attacked area of the lower sample in Fig. 2.

The mechanism behind the increased sensitivity towards methylene chloride resulting from electron irradiation is not known. Ionizing radiation may react with the sample in many different ways (6). In most cases it is difficult to tell whether beam damage is primarily caused by beam heating or by chemical changes brought about by the ionizing radiation (7). In this study it was found that substituting the air in the sample chamber by nitrogen did not affect

the beam damage. This indicates that chain scission induced by peroxide formation does not play a dominant role in the present case.

CONCLUSION

By combining electron irradiation with the methylene chloride test it is possible to arrive at a quantitative value expressing the level of gelation for well gelatinized rigid PVC. The method can also be used to test the uniformity of the gelatinization process.

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TABLE 1. Irradiation conditions.

Acceleration voltage 35 keV

Specimen chamber pressure: 50 N/m²

Beam current (i): 0.35-28.0 10⁻¹¹ A

Irradiation time: 120 s

Irradiated area: 2.9 10⁻⁵ cm²

Exposure: 0.15-11.6 10⁴ Q/cm²

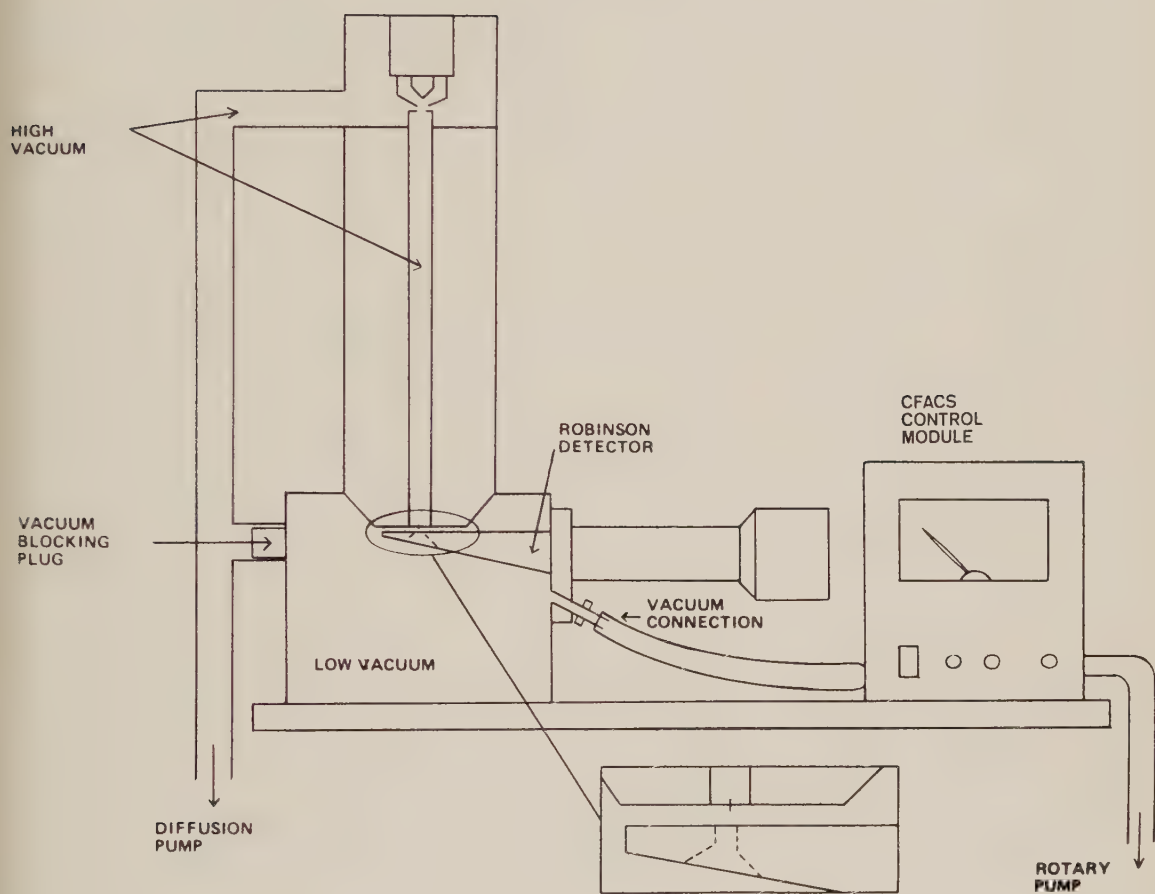


Figure 1. A scanning electron microscopy fitted with a Robinson detector and an environmental cell.

Level of gelation
(Wavinorm 14.001)

The exposure (Q/cm^2)
at an increased attack
of methylene chloride

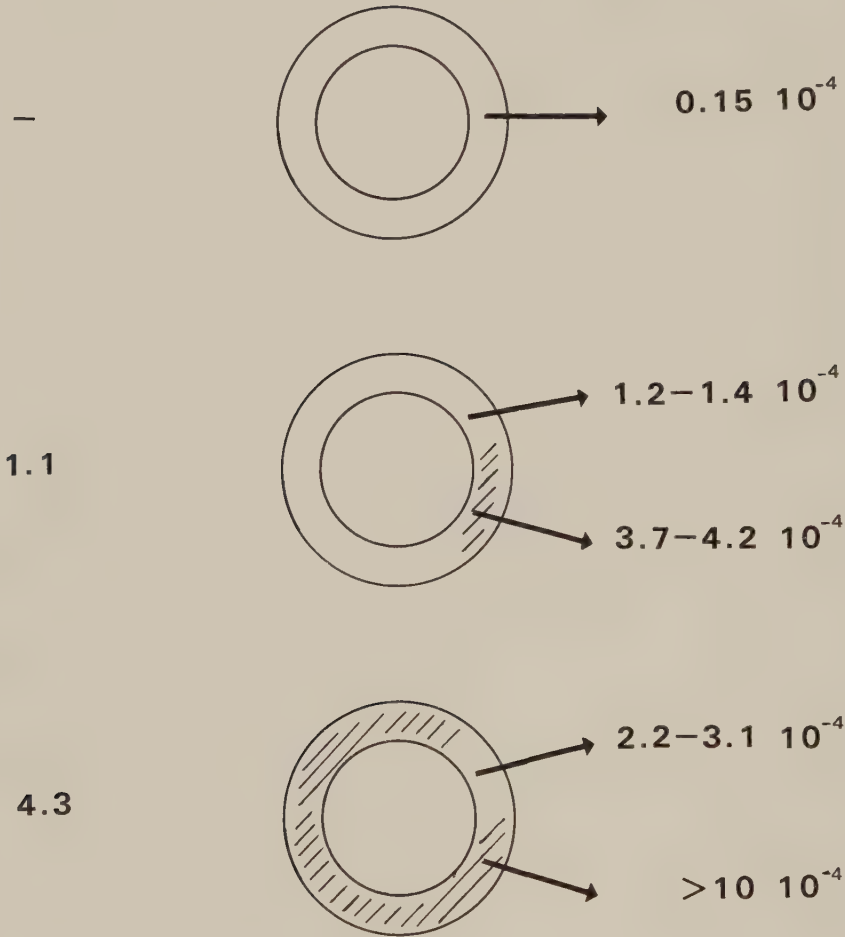


Figure 2. Results from methylene chloride tests and methylene chloride tests and methylene chloride tests in combination with electron irradiation.

